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The Theory and Practice of Sodium Chlorite Bleaching

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The decomposition of sodium chlorite during the bleaching of flax has been studied at different pH values and various temperatures. Bleaching with sodium chlorite should be accompanied by maximum formation of sodium chloride and minimum formation of sodium chlorate and chlorine dioxide. The oxidising power of the bleaching agent is discussed. Whilst there is a good margin of safety with sodium chlorite under normal bleaching conditions, extreme conditions must be avoided, in order to prevent chemical damage. The effect of sodium chlorite on the impurities present in cotton and flax is discussed. The use of hot, weakly acid oxidising solutions permits shortened bleaching processes.

The main problems in practical sodium chlorite bleaching are (1) choice of a suitable method of activation of the bleaching agent, (2) selection of corrosion-resistant materials for construction of bleaching plant, and (3) design of the equipment to be used.

Introduction

Sodium chlorite, under the name *Textone*, was first introduced as a commercial bleaching agent for textile fibres in 1939, by Mathieson Alkali Works in the United States. It is now produced on an industrial scale in the United States, France, and Germany, and a plant for its manufacture is being constructed in Great Britain by Laporte Chemicals Ltd. One of the most important considerations affecting the use of sodium chlorite is the economic factor. Commercial anhydrous sodium chlorite of 80% strength costs 39–40d. per lb. at present in the United Kingdom, which entails higher chemical costs in most bleaching processes, in comparison with hypochlorites or peroxides. Significant advantages in other directions are therefore necessary in order to offset high chemical costs. Chlorite bleaching of cotton and linen can be safer and shorter than conventional bleaching techniques. Of particular interest is the reduction in the severity, or possible omission, of the traditional alkaline kier-boiling processes. Sodium chlorite can also be used to bleach regenerated and synthetic fibres and blends. It has not been used in bleaching wool or protein fibres. The introduction of chlorite has raised problems associated with corrosion of equipment and evolution of the troublesome heavy gas, chlorine dioxide. It is desirable to employ conditions which give most efficient use of the bleaching agent, no risk of corrosion of plant, and no contact of personnel with chlorine dioxide gas.

Properties of Sodium Chlorite

Most commercial forms of anhydrous sodium chlorite have ca. 80% active material. A typical analysis[1] of sodium chlorite (Elektrochemische Werke, München) is—

	%
Sodium chlorite	⩽80
Sodium chlorate	1·5–3·0
Sodium chloride	12·0–13·5
Sodium carbonate	2·5
Sodium hydroxide	0·5
Water	0·5

Solid sodium chlorite has good storage stability. It undergoes no decomposition until heated above 175°C., when sodium chlorate, sodium chloride and a small amount of oxygen are produced[2]. However, decomposition is accelerated by the presence of organic matter, and a mixture with organic material has a much lower ignition temperature. Indeed, care must be taken in the storage of chlorite to avoid fire hazards.

Sodium chlorite is readily soluble in water, e.g. a 39% (wt./vol.) solution is obtained at 17°C., and the commercial forms give an aqueous solution of pH 10. Alkaline solutions are stable, but with decrease in pH and increase in temperature the solution becomes greenish yellow, liberates chlorine dioxide gas, and sodium chloride and chlorate are found in the solution[2]. Solutions which are acid, or capable of developing acidity on heating, are used in textile bleaching.

Theory of Sodium Chlorite Bleaching

DECOMPOSITION DURING BLEACHING

Hefti, in 1955, published a study of sodium chlorite decomposition in solution at pH 1·6–5·95 and 40–80°C. in the presence and absence of cotton[3]. The decomposition products measured included chloride, chlorate, chlorine dioxide in aqueous and gaseous phases, and oxygen. Chlorine gas and hypochlorite ions were not detected. It was shown that lower pH values and higher temperatures increased the speed of decomposition, giving increased amounts of chlorine dioxide, chloride, and chlorate. Formation of chlorine dioxide was shown to be the main reaction in the acid decomposition of chlorite and was at a maximum at pH 2·5–3·0. Appreciable quantities of chloride and chlorate were found at pH <4·0. It was concluded that the decomposition reactions were not affected by the presence of kier-boiled cotton, which must have contained substantially no impurities except colouring matter.

It was suggested that sodium chlorite in acid solution decomposed as follows—

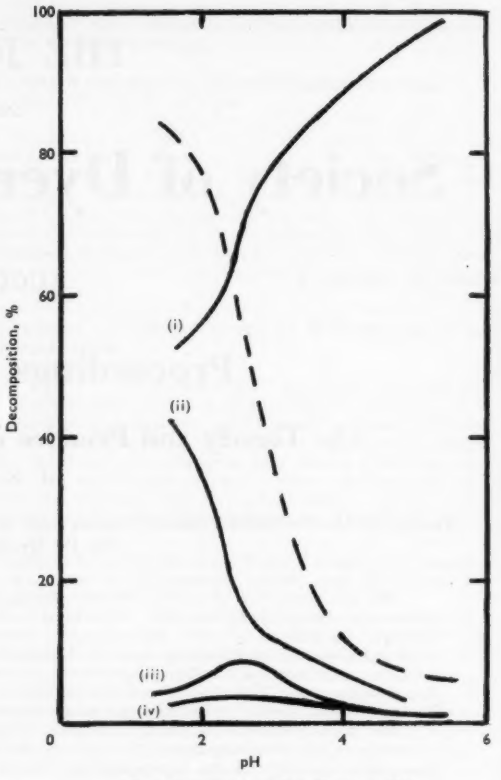
$$5ClO_2^- + 2H^+ \rightarrow 4ClO_2 + Cl^- + 2OH^- \quad (i)$$

$$3ClO_2^- \rightarrow 2ClO_3^- + Cl^- \quad (ii)$$

$$ClO_2^- \rightarrow Cl^- + 2O \quad (iii)$$

The calculated contribution of each of these reactions to the total chlorite decomposition is illustrated in Fig. 1. Reaction (i) was shown to be the principal one, but its importance decreased with fall in pH. Reaction (ii) commenced below pH 4·8 and became more important with fall in pH. Reaction (iii), which occurred only to a small extent, took place only in acid solution and was at a maximum at pH 2·4. It was observed that less oxygen was evolved when cotton was present, so it was assumed that part of the atomic oxygen liberated was taken up by the cotton cellulose or its impurities. Confirmation of this was suggested by the measured greatest degree of bleaching, which occurred at pH 2·4, with maximum formation of carboxyl groups in the cellulose. Hefti therefore suggested that sodium chlorite bleached through formation of atomic oxygen, and that neither chlorine dioxide nor the chlorite ion, as such, was the effective bleaching agent.

Complete confirmation of this theory requires polarographic evidence, which may help to establish the active species responsible for the bleaching action. Other workers have demonstrated that the chlorite ion, or an active species derived from it,



— — Total decomposition after 60 min. at 60°C.
(i) Contribution of reaction (i) to total decomposition, measured both for the blank and in presence of cotton
(ii) Contribution of reaction (ii), both for blank and in presence of cotton
(iii) Contribution of reaction (iii), blank only
(iv) Contribution of reaction (iii), in presence of cotton

FIG. 1— Calculated Percentage Contribution of Different Reactions in the Breakdown of Sodium Chlorite in Solutions of Different pH Values (Hefti [3])

is the effective oxidising agent, rather than chlorine dioxide [4–8].

The decomposition of sodium chlorite in the presence of flax yarn buffered at different pH values at 80°C. has been studied by the present author (Table I). Results obtained after 120 min. are illustrated in Fig. 2. The presence of grey flax accelerates or activates the decomposition of sodium chlorite at pH <7·0 when bleaching commences at 80°C. Clearly, formation of sodium chloride is the most important final decomposition

TABLE I

Effect of pH and Time on the Decomposition of Sodium Chlorite Solutions at 80°C.

BLANK SOLUTIONS

	pH 2·0			pH 3·0			pH 4·0			pH 5·0			pH 6·0			pH 8·0			pH 10		
	Cold	80°C. 60 min.	80°C. 120 min.	Cold	80°C. 60 min.	80°C. 120 min.	Cold	80°C. 60 min.	80°C. 120 min.	Cold	80°C. 60 min.	80°C. 120 min.	Cold	80°C. 60 min.	80°C. 120 min.	Cold	80°C. 60 min.	80°C. 120 min.	Cold	80°C. 60 min.	80°C. 120 min.
Measured pH	2·13	2·97	2·73	3·19	3·88	4·00	4·02	4·48	4·53	5·13	5·27	5·36	6·27	6·71	6·99	8·14	7·97	8·04	9·90	9·86	9·98
Sodium chlorite, g./litre	3·82	1·36	1·12	3·98	2·24	1·60	4·02	3·40	3·02	3·98	3·80	3·72	3·96	3·94	3·92	3·90	3·86	3·86	3·96	3·90	3·98
Sodium chloride, g./litre	0·78	1·32	1·36	0·66	1·04	1·26	0·66	0·80	0·90	0·64	0·66	0·68	0·64	0·66	0·66	0·66	0·66	0·64	0·67	0·66	0·66
Sodium chlorate, g./litre	0·14	0·74	0·96	0	0·22	0·76	0	0	0	0	0	0	0	0	0	0	0	0	0	0	0

FLAX YARN PRESENT

Measured pH	2·03	2·97	2·97	3·26	3·70	3·45	4·36	4·29	4·23	5·14	4·99	4·96	6·58	6·06	5·92	7·32	7·10	7·08	10·28	9·56	9·59
Sodium chlorite, g./litre	3·62	1·08	0·66	3·96	0·86	0·30	3·96	1·38	0·76	4·04	2·72	2·10	3·98	3·46	3·18	3·92	3·72	3·62	3·96	3·82	3·80
Sodium chloride, g./litre	0·78	3·28	3·44	0·66	2·42	2·76	0·66	1·90	2·22	0·64	1·36	1·68	0·66	0·96	1·12	0·68	0·84	0·90	0·64	0·74	0·80
Sodium chlorate, g./litre	0·16	0·44	0·56	0	0·78	1·22	0·10	0·40	0·52	0·02	0·38	0·30	0	0·06	0·02	0	0	0	0	0	0

TABLE II

Effect of pH on Fluidity and Whiteness

pH	2·0	3·0	4·0	5·0	6·0	7·0	10·0	Grey Yarn
Fluidity	8·1	7·7	6·3	4·6	4·1	3·5	4·2	3·5
Reflectance, %*	81	76	68	72	58	43	40	21

* EEL absorptiometer, against magnesium carbonate

reaction in the bleaching action of chlorite. Formation of sodium chlorate and evolution of chlorine dioxide at low pH values indicate loss of valuable bleaching agent.

The fluidity of the treated flax yarn rises at pH values below 4·0 and is accompanied by greater whiteness (Table II), as well as more complete decomposition of the chlorite in solution and pronounced evolution of chlorine dioxide.

The decomposition of sodium chlorite was similarly studied at 96° and 121°C. under alkaline, neutral, and weakly acid conditions. Results after 120 min. are illustrated in Fig. 3. The reaction is accelerated by rise in temperature to 96° and 121°C., and at the latter temperature a bleaching effect is obtained at neutral pH values, but there is a tendency for higher fluidity figures to be produced (Table III). In these experiments more sodium chlorite was used than is required for practical bleaching, and the higher fluidity figures reported at pH <4 and temperatures above 96°C. may not necessarily be reproduced under all conditions. The results merely indicate that a smaller margin of safety existed under these conditions.

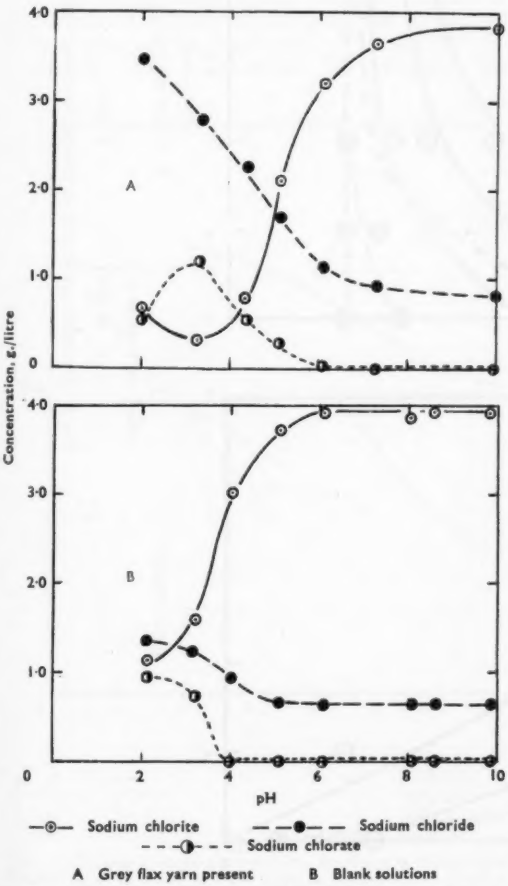


FIG. 2— Decomposition of Sodium Chlorite Solutions at Different pH Values in Presence and Absence of Grey Flax (at 80°C. for 120 min.)

TABLE III

Effect of Time, Temperature and pH on Fluidity and Whiteness

pH	Time (min.)	96°C. Reflectance (%)	96°C. Fluidity	121°C. Reflectance (%)	121°C. Fluidity
5	120	78	5·0	68	7·2
6	120	80	4·0	70	7·0
7	60	—	—	59	6·8
7	90	—	—	61	6·8
7	120	57	3·7	66	7·9
10	120	36	4·7	42	8·5

Theoretically, the optimum conditions for using acidified chlorite should be those which promote—

(*a*) Maximum formation of sodium chloride

(*b*) Minimum formation of chlorine dioxide

(*c*) Minimum formation of sodium chlorate.

These conditions appear to occur in the region pH 4–7, in which evolution of chlorine dioxide is low. At pH values below 4, and particularly at pH 2·4, loss of bleaching capacity through decomposition with formation of chlorine dioxide is excessively high. By controlling the pH in the range 4–7 this loss is prevented, and the problem then centres on finding a suitable catalyst to promote the type of decomposition which gives the maximum bleaching effect.

OXIDATION POTENTIAL

Colour in organic compounds is associated with the presence of mobile π electrons in a conjugated double-bond system. When these electrons are immobilised by breakdown of the conjugated system, the chromophoric system is destroyed and bleaching takes place. Oxidising agents such as hydrogen peroxide, sodium chlorite, and hypochlorites are electron-acceptors, and their oxidising power is quantitatively measured by the oxidation potential. Oxidation potentials may be calculated for probable rate-determining reactions, referring the potentials to the standard hydrogen/hydrogen-ion potential as zero (Fig. 4) [9].

In practice, although the potential of an oxidising solution can be measured, e.g. by using a platinum electrode and a calomel half-cell, this potential cannot be identified with a particular oxidation reaction in many cases, since the measured potential depends not only on the standard potential, but also upon the ionic concentrations, which may not be known. Furthermore, several oxidation processes may be occurring simultaneously. Hence the measured potential

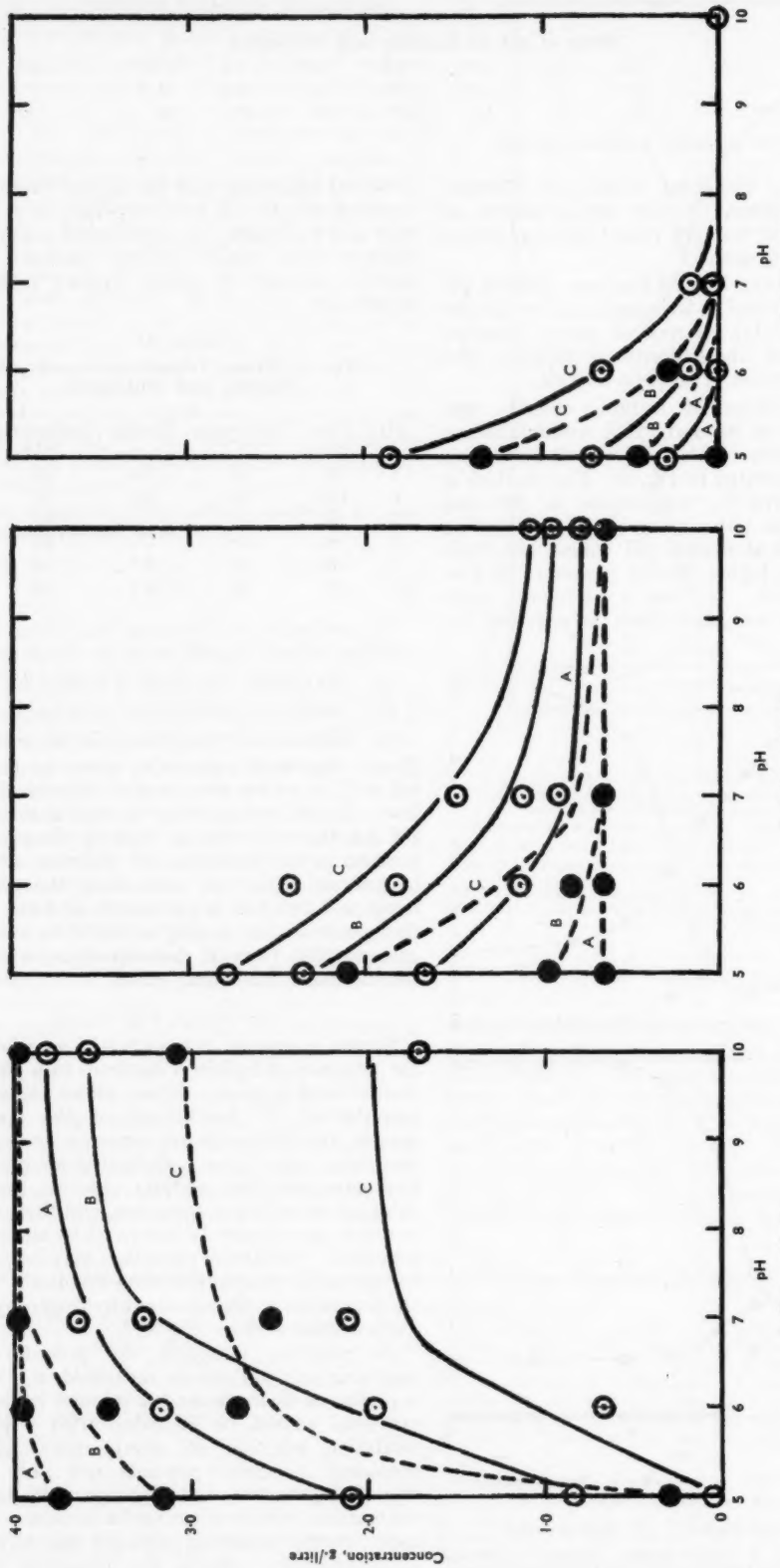


FIG. 3— Decomposition of Sodium Chlorite Solutions of Different pH Values after 120 min.

TABLE IV

Composition (%) of Retted Flax and Cotton

	Cellulose	Hemicellulose	Pectin	Lignin	Fats and Waxes	Water-solubles	Moisture	Total Impurities
Retted flax	64·1	16·7	1·8	2·0	1·5	3·9	10·0	25·9
Cotton	82·7	5·7		—	0·6	1·0	10·0	7·3

does not represent the absolute oxidation potential for the system [10]. However, this type of measurement confirms in general the calculated values for selected reactions shown in Fig. 4.

For the selected oxidation reactions it is clear that oxidation potential varies with pH, and that hypochlorite solutions (which contain varying amounts of chlorine, hypochlorous acid and hypochlorite ions [9]) have the highest potential at all pH values. Alkaline peroxide solutions have a considerably lower oxidation potential, whilst acid sodium chlorite solutions are intermediate in value [2]. The fact that acid chlorite solutions (pH 4–7) have lower oxidation potentials than alkaline hypochlorite solutions (pH 10–11) has been taken to indicate that there is less risk of chemical damage when bleaching with chlorite. This has been demonstrated by several workers [3, 11, 12]. It is noteworthy that, whilst pH has a considerable influence on oxidising power, the rate of oxidation also varies with concentration of the agent and temperature of the treatment. Hence pH, concentration and temperature all influence the activity of the bleaching agent and must be carefully controlled. Chemical damage to cotton was shown to occur when very high concentrations of sodium chlorite, viz. 60 g./litre, were used at pH 5 and 80°C. for at least 20 hr.[13]. In practice much milder conditions will suffice to bleach cellulosic fibres; there is then no danger of degradation, and a considerable margin of safety exists in controlling the process.

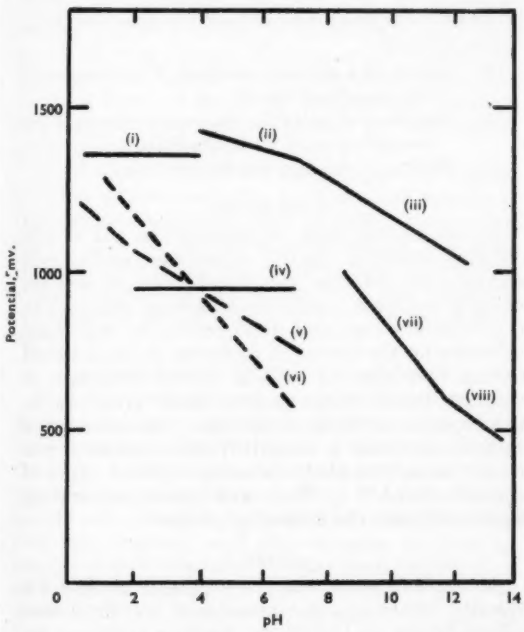


FIG. 4—Calculated Oxidation Potentials for Selected Reactions of Hypochlorites, Chlorites, and Peroxides in pH Ranges of Practical Importance (Holst [9])

EFFECT OF SODIUM CHLORITE ON IMPURITIES PRESENT IN COTTON AND FLAX

The impurities in flax and cotton are similar in kind, but vary greatly in amount (Table IV) [14].

By extracting individual impurities [15] and bleaching the extracted yarn containing different impurities (Table V), acid sodium chlorite was shown to bleach all the impurities present in flax yarn. The results shown in Table V confirm the conclusion that impurities in grey flax activate the decomposition of sodium chlorite under bleaching conditions (Fig. 2). As the impurities present in flax and cotton are of related types, grey cotton should also activate the decomposition of chlorite, but to a lesser extent than flax. This is, in fact, observed in practice.

TABLE V

Effect of Impurities on Bleaching

Impurities Present	Reflectance (%) Before Bleaching	After Bleaching*
Lignin	55	83
Lignin and hemicellulose	28	68
Lignin, pectin and hemicellulose	30	65
Lignin, pectin, hemicellulose and water-solubles	22	65
Grey flax yarn	21	68

* 5 g. sodium chlorite (80%) and 2 ml. formic acid (100%) per litre, at 80°C. for 2 hr., liquor ratio 20 : 1.

The most significant feature about the bleaching action of hot acid chlorite is that a single treatment bleaches directly the lignin present in the woody matter ("sprit") which is found in flax and is also associated with the particles of seed and husk ("motes") that are especially obvious in certain qualities of cotton. In conventional processes flax sprit can be decolourised by chlorination followed by an alkaline treatment, whilst in cotton a caustic pressure boil followed by an alkaline hypochlorite treatment will usually bleach motes.

The introduction of sodium chlorite permits shorter bleaching processes, especially in regard to kier boiling. Weight-losses are lower, compared to those caused by conventional processes in which almost all the impurities are removed. However, the problem of absorbency and removal of wax

TABLE VI

Effect of Chlorite Bleaching on Wax Content of Grey Flax Yarn

Treatment	Untreated	Water (2 hr. at 80°C.)	5 g./litre Sodium Chlorite (80%) (2 hr. at 80°C.) at—						
			pH 2	pH 3	pH 4	pH 5	pH 6	pH 7	pH 10
Wax content, %	1·40	1·08	0·95	0·63	0·71	0·74	0·71	0·67	0·82

then becomes important. The hot chlorite treatment is carried out at temperatures above the melting point of the mixture of natural fats and waxes present. With flax, the benzene extract from grey yarn is a very dark brown hard wax, m.p. 63–66°C., and chlorite treatments at 80°C. in the absence of added emulsifying agents remove ca. 50% of the wax present (Table VI).

Addition of selected, stable emulsifying agents has been recommended for aiding the removal of wax in hot chlorite baths.

It was observed that the chlorite solutions used for bleaching grey flax yarn (Table VI) gave a precipitate of a white solid on cooling or on dilution with cold water. In order to determine the nature of this precipitate, the chlorite solutions, employed to bleach flax yarns with different impurities selectively removed (Table V), were decanted at the end of bleaching and allowed to cool. The solution from the grey flax gave an appreciable amount of white solid. A much smaller amount of white solid was present in solutions used to bleach yarn with (*a*) wax and (*b*) wax plus water-solubles removed. In contrast, solutions from the treatment of yarns with (*c*) wax, water-solubles and pectins removed, and (*d*) with wax, water-solubles, pectins and hemicelluloses removed, both deposited no precipitate on cooling. This demonstrated that most of the insoluble matter likely to be precipitated by cooling the bleaching solutions was bleached wax, with smaller amounts of material soluble in hot water, and pectin. As the acid chlorite solution at the end of bleaching contains a suspension of molten waxes, carefully controlled hot washing off is necessary in order to avoid precipitation of suspended wax on to the material.

Absorbency in cotton and linen bleaching is greatly improved by a short alkali treatment, either before or after the hot chlorite stage. The actual position of the alkali scour, or steep, depends on the degree of whiteness and absorbency required, and may influence the concentration of chlorite necessary to obtain a satisfactory bleach. White, Ross, and Crowder[16] have commented on wax removal from chlorite-bleached cloth. They compared the absorbency of cotton fabric which had been solvent-dewaxed and chlorite-bleached with that of cloth which had been either chlorite-bleached only or bleached and then treated with alkali. The dewaxed sample had superior absorbency in every case, and retained this property on heating. The alkali-aftertreated sample had considerably decreased absorbency when heated, but was superior to the sample which had only been chlorite-bleached.

Shorter alkali treatments, in which smaller amounts of alkali-soluble impurities are removed (particularly hemicellulose in flax), impair the stability of the white obtained. Hvattum and Turner[17] have pointed out that the presence of hemicellulose in bleached cloth can cause yellowing on storage, especially if the cloth is heated. This lack of stability may not be completely counteracted by adding fluorescent brightening agents. It is possible that the terminal aldehyde groups present in short-chain hemicellulose molecules may be the cause of this yellowing. For example, it has been shown that α-glucose yellows when condensed with urea–formaldehyde, whilst methyl α-glucoside remains colourless under the same conditions[18]. If in sodium chlorite bleaching, conditions could be established in which free aldehyde groups in the retained hemicelluloses were oxidised, superior stability of the white might be obtained.

Practical Sodium Chlorite Bleaching

The conditions for sodium chlorite bleaching of cellulosic fibres which have become accepted are—pH 4–7, at 60–100°C., for times varying from 30 min. to 6 hr.; with concentrations up to 5 g./litre in long liquors, and in padding processes, 20–30 g./litre for cotton and as high as 70 g./litre for linen. Suitably chosen conditions cause no measurable oxidative damage to natural and regenerated cellulosic fibres, and polyamide, polyester, and acrylic fibres can also be bleached. The main problems associated with sodium chlorite bleaching in practice are—

(1) Choice of a suitable method of activation of the bleaching agent
(2) Selection of suitable resistant materials for construction of bleaching plant
(3) Design of suitable machinery.

ACTIVATORS

Agents of this type (*a*) control the pH of the chlorite solution during bleaching and/or (*b*) activate or catalyse the breakdown of sodium chlorite to give a maximum bleaching effect. The type of activating agent employed has an important influence on the extent of corrosion to be expected during bleaching, as well as on the evolution of chlorine dioxide (density 2·4), which gives rise to troublesome working conditions. Selection of a suitable activator is a controversial question, and claims have been made for many different types of compounds[7, 8, 19]. The well-known activating agents fall into the following groups—

Acids

Acidic activation, the conventional method for chlorite bleaching, was introduced by Mathieson Alkali Works in 1939[20–23]. Various acids can be added to control pH between 3 and 5, e.g. phosphoric, acetic or formic acid. Hydrochloric and oxalic acids are avoided because of their corrosive action on stainless steel. pH values below 3·5 are not used, because of the evolution of excessive amounts of chlorine dioxide and risk of corrosion,

but pH values below 4 have been recommended for bleaching synthetic fibres. Chemstrand have patented a process in which acrylic fibres are bleached by treatment in hot dilute sulphuric acid at 93°C. followed immediately by sodium chlorite solution at 71–82°C. for 45 min.[24]. Terylene can be bleached with almost boiling sodium chlorite solution acidified to pH 2–3 with nitric acid[25], whilst nylon can be bleached with sodium chlorite at pH 2·5–3·5 in presence of formic, acetic or nitric acid, at 60–90°C. for 30–120 min.[26].

Sodium Salts

Various sodium phosphates (sodium dihydrogen phosphate[8], disodium hydrogen phosphate[27], sodium polyphosphates[27], disodium pyrophosphate[8], tetrasodium pyrophosphate[28]), as well as sodium formate[29] and sodium acetate, have been recommended. These are buffer salts which stabilise the pH during bleaching. They are also claimed to control evolution of chlorine dioxide and protect stainless steel from corrosion. Deutsche Gold- und Silber-Scheideanstalt (Degussa) advise the addition of tetrasodium pyrophosphate to a formic acid-activated chlorite bath for this purpose[28].

Borezee and Chary[8] found that a solution of commercial sodium chlorite containing no activator had pH ca. 10. This solution, when applied to cotton by the pad–steam process, underwent decomposition at 95–100°C. The pH fell to 8·5, when bleaching commenced, and continued falling to a steady value of 5·0. After steaming for 3–4 hr. the cotton was completely bleached and negligible amounts of chlorine dioxide were evolved. It was found that disodium dihydrogen pyrophosphate was the most suitable buffer salt and brought the pH to 7·2 before bleaching commenced. Sodium dihydrogen phosphate could also be used, but it gave less bleaching effect.

With neutral buffer activators, speed of decomposition of the chlorite is slow and relatively concentrated solutions must be used. It has been shown that a pad–steam sequence is the most efficient, giving ca. 80% consumption of chlorite, whilst for immersion treatments a standing bath is preferable, as only 60% of the chlorite is used up[8].

Hydrolysable Organic Compounds

Organic ester activators, particularly diethyl tartrate and ethyl lactate, have been patented by Société Rhodiaceta[30]. Other compounds, particularly mono- and di-polyalcohol esters and lactones, have been examined by Mosse[7]. Ethyl lactate was selected for pad–steam bleaching, for economic reasons, and also because it gave no evolution of chlorine dioxide after bleaching for 2 hr. at 100°C., although the pH fell from 7·5–7·7 to 5·0–6·5. Ethyl lactate was preferred for use in long liquors. As with neutral buffer salts, which operate in a similar pH range, hydrolysable organic esters cause slow decomposition of chlorite and promote excellent bleaching, but higher temperatures and more concentrated chlorite solutions are required than when acid activators are used. The advantages of ester activators are minimum evolution of chlorine dioxide, less danger of corrosion of stainless steel in the pH range 5–7, and better working conditions[19, 31, 32].

Many other organic compounds which develop acidity on heating can be added to chlorite baths. One example is sodium chloroacetate, which is in commercial use; it hydrolyses during steaming with formation of hydrochloric acid and glycollic acid in the material. Economic factors will probably decide which compounds are developed for commercial bleaching.

Ammonium Salts

Patents have been granted for the addition to chlorite baths of ammonium salts, viz. ammonium chloride, sulphate, and chlorate; ammonium salts of aliphatic carboxylic acids[33]; and ammonium bifluoride[8], which has a buffer effect at pH 3–5 and can be used in long liquors for bleaching synthetic and regenerated fibres. Ammonium dihydrogen phosphate has been shown to give final pH values of 5·3–5·8, with less formation of chlorine dioxide and less corrosion of stainless steel at 95°C. than in acid-activated chlorite baths[19].

In the Stoffel process[34], addition of ammonium salts, or salts of organic bases with strong organic or inorganic acids, is recommended for pad–steam techniques; the ammonia liberated is claimed to reduce corrosion of stainless steel.

Peroxygen Compounds

Hydrogen peroxide may be added to acidified chlorite solutions to reduce evolution of chlorine dioxide and protect stainless steel in cotton bleaching[35]. Borezee and Chary[8] showed that, in neutral chlorite bleaching of cotton, using disodium dihydrogen phosphate in long liquors, any evolution of chlorine dioxide could be stopped by adding a little hydrogen peroxide. Degussa have patented a double process, using a mixture of sodium chlorite and hydrogen peroxide, carried out first under acid and then under alkaline conditions[36]. Persulphate can also be used[35].

Sodium Hypochlorite

Addition of sodium hypochlorite to sodium chlorite in alkaline solution (pH 9–10) was one of the original methods proposed by Mathieson Alkali Works[12, 22, 37]. It is now accepted that hypochlorite is the effective bleaching agent in such a mixture[38], and economic factors mitigate against application of this process.

Other Methods

Aldehydes, particularly formaldehyde, have been proposed as activators in acid or alkaline chlorite solutions[5, 12, 23, 39]. Amides, e.g. chloroacetamide, can also act as activating agents[40]. Certain metallic salts, viz. cobalt, nickel, and manganese salts, can activate chlorite in neutral solutions at low temperatures[41]. Other patents cover the addition to chlorite solutions of sulphur or selenium in a fine state of division[42], or trichloroethylene[43].

Activating agents of the acid, acid salt, hydrolysable organic ester, and ammonium salt

types are the main ones used commercially in textile bleaching. The efficiency of any chosen activator in promoting maximum bleaching is of vital importance in ensuring economy in the use of the bleaching agent. The bleaching method employed, i.e. the use of long or short liquors, or the pad–steam technique, has a considerable influence on the choice of activator. Further, an activating agent suitable for use under one set of bleaching conditions may not give the best results for all other conditions.

CORROSION

In general, acid chlorite solutions at pH 4 and 80–100°C. attack iron, copper, nickel and their alloys. Pure aluminium with a coating of oxide, lead with a coating of sulphate, and wood have some resistance, whilst glass, ceramic linings, stoneware, glazed earthenware, and titanium [7, 44] are completely resistant. Certain plastics have good resistance, particularly polytetrafluoroethylene, polypropylene, high-density polyethylene, and selected cross-linked polyester, glass-reinforced mouldings; other polymers are resistant, but become thermoplastic above 70°C. [45, 46]. The coating of metals with resistant plastics or paints has not been widely accepted as a satisfactory solution to the corrosion problem.

Most interest has centred on the corrosion-resistant stainless steels (Table VII). Normal grades of austenitic stainless steels with 18% chromium and 8% nickel are attacked, but the presence of 2–5% molybdenum in the steel has been found to impart better resistance. In 18/8 stainless steels the chromium imparts the property of forming surface oxide films which are very thin, dense, adherent, self-healing, and passive. The addition of nickel is required to maintain the austenitic structure at room temperature. In such a steel the carbon content must be kept low in order to form a completely solid solution, or one-phase type of structure, which has high resistance to electrolytic attack. The addition of small amounts of molybdenum overcomes weld decay due to carbide precipitation, which can arise from faulty heat-treatment, and provides the stainless steels of highest general corrosion-resistance. The resistance to corrosion depends on the presence of the invisible surface oxide film, and its thickness and chromic oxide content increase with the degree of polish. The following properties influence the chemical resistance of the oxide film—

(1) Thickness and impermeability
(2) Adherence to the metal
(3) Mechanical strength
(4) Ability to repair defects in the oxide film by self-healing.

Clearly, for maximum resistance, cleanliness of the surface is essential, and the surface polish should be kept as bright as possible. The molybdenum-containing grades of stainless steel, particularly the 18/10/3 Cr/Ni/Mo grade, have good resistance to oxidising media, e.g. nitric acid or alkaline hydrogen peroxide, in which any defect in the surface oxide film, which may have arisen through abrasion, is quickly repaired. Chromates and phosphates also promote repair of the oxide film, but chlorides and sulphates are especially liable to cause breakdown of the film. Even under oxidising conditions, halide ions can penetrate the passive film easily and cause local breakdown or pitting. Thus, even the molybdenum-containing grades have only limited resistance to hypochlorites and sodium chlorite, which contain appreciable amounts of chloride ions. Occasional passivation treatment, e.g. with 10–20% nitric acid solution at 25–60°C. for 10–30 min., is essential in order to re-form the surface oxide film and to obtain maximum resistance with this type of stainless steel [47].

The stainless steel grade *V4A supra*, which contains 2·8% molybdenum, has been used by German machinery manufacturers and is recommended for use with acid chlorite solutions, providing (*a*) buffers are added to keep the pH above 3·8, (*b*) the temperature does not exceed 80°C., (*c*) sodium nitrate or nitric acid is added to the bleaching solution to act as a corrosion-inhibitor, and (*d*) periodical passivation with nitric acid is carried out. The use of nitric acid and sodium nitrate as corrosion inhibitors for V4A grade stainless steel has been patented [48]. Hoechst make a special grade of sodium chlorite containing 50% sodium chlorite and 50% sodium nitrate especially for use in stainless steel equipment, e.g. package-bleaching plant. Degussa recommend the use of sodium pyrophosphate for a similar purpose [28]. The use of corrosion-inhibitors in chlorite baths is widely recommended with stainless steel plant, but, whilst formation of visible pitting or rusting may be prevented, invisible corrosion may still

TABLE VII

Constituents of Different Types of Stainless Steels

Type				Constituents (%)						
Krupps	B.S.	Staybrite	Silver Fox	Cr	Ni	Mo	Mn	Si	Ti	C
—	En.58J	FMB	316	18	10	3	0·8	0·3	—	0·07
—	En.58J	FMB. Ti	835	18	10	3	1·5	0·3	0·3	0·07
—	—	FML	25	18	10	1	0·8	0·3	Trace	0·07
—	En.58B	FDP	22	18	8	—	1·75	0·8	0·6	0·10
—	En.58E	FSL	—	18	10	—	0·8	0·6	—	0·05
V4A Extra	—	—	—	18	10	2	0·3	0·4	—	0·12
V4A Supra	—	—	—	18	10	2*	0·3	0·4	*	0·07
V14A Supra	—	—	—	17	13	4·7	0·3	0·4	—	0·07
V2A	—	—	—	18	8·5	—	0·3	0·4	—	0·15

* The figure for Mo includes some Ti

proceed, particularly if a slight dulling of the polished surface can be detected. If general corrosion of this type arises, penetration should not exceed 0·005 in. per year, which would reduce a 10SWG sheet to half-thickness in ten years.

Polarisation of molybdenum-containing grades of stainless steel has also been mentioned as a means for giving additional protection against acid chlorite solutions [7]. It can be carried out by immersing an aluminium sheet in the acid chlorite solution and connecting it, outside the liquor, to the wall of the vessel. The aluminium dissolves in place of any of the components of the stainless steel.

The degree of corrosion of a selected stainless steel occurring in practice will depend on the concentration, the temperature and pH of the chlorite solution, the type of activator added, and the evolution of chlorine dioxide. Sufficient information is now available about these factors, and about the action of corrosion-inhibitors and passivation treatment, to enable bleaching conditions which will minimise corrosion to be chosen. The attack on stainless steel is threefold, viz. below the liquor line, at the liquor line, and above it. Attack is most severe at the air–liquid interface, but, together with the attack below the surface, can be controlled by the methods discussed. Attack above the surface is probably due to chlorine dioxide, and its evolution must be minimised by suitable activation of the bleaching solution. If processes which re-form surface oxides, e.g. alkaline peroxide treatments, are given in the same plant, the corrosion by acid chlorite solution will be further reduced.

BLEACHING PLANT

Yarn

The introduction of sodium chlorite for bleaching linen yarn has coincided with a change from processing in hank to processing in package form, i.e. in cheese or cone. In the last four years these changes have revolutionised linen yarn bleaching in the United Kingdom, although package bleaching has been practised on the Continent for some time. Krantz and Longclose open machines are used at temperatures up to 95°c., whilst the closed Thies and Obermaier machines can be used at temperatures up to 120°c. The process can include an alkali boil or steep, chlorination or acid chemic, alkaline hydrogen peroxide, and acid sodium chlorite, the complete bleaching process being completed in 8–12 hr.

Cloth

Two main types of chlorite bleaching processes are available, viz. (*i*) treatment in rope form by immersion or saturate-and-steam sequences, and (*ii*) the open-width pad–steam sequence.

Treatment in Rope Form— Wooden, tile-lined, glass fibre-reinforced polyester resin, or stainless steel enclosed winches and modified kiers and J-boxes may be used. A system for modifying existing kiers has been introduced by Degussa. Open kiers are lined with small stoneware tiles, e.g. those made by Deutsche Steinzeugwarenfabrik Friedrichsfeld (DSF). The external circulation system may comprise stoneware pipes with iron reinforcement, a stoneware centrifugal pump and direct injection with high-pressure steam. The delivery pipe of the circulation system is mounted laterally close to the upper edge of the kier. A de-aerating pipe is fitted to the side of the kier to remove air which may collect in the bottom of the vessel. A wooden or glass fibre-reinforced polyester lid seals the top and is attached to cross beams held on to the kier by four swivel clips. A perforated wooden platform adjustable for height is attached under the lid and holds the cloth down during bleaching. This type of modified kier can be used to advantage in cotton bleaching by the Degussa system, in which the singed and desized fabric is treated at 80–90°c. with 1·2–1·5% sodium chlorite (on the weight of cloth) at pH 4·0 for 3–4 hr., washed, given a short alkali scour at 90–95°c. to complete the removal of waxes, and rinsed [49].

Continuous rope bleaching of cotton with sodium chlorite can be carried out by the Degussa system in plant constructed by DSF. The desized and washed fabric is saturated with the chlorite solution, squeezed, preheated, and steamed at 95°c. for 90 min. in a J-box of the du Pont type. The equipment is constructed of large sections of stoneware reinforced with iron. One plant of this type is operating in England with cotton interlock [50].

Open-width Bleaching— Whilst enclosed jigs are the simplest form of equipment, many machines using the sequence— pad, heat, and batch in an insulated chamber— have been introduced. Typical examples are constructed by Svenska in Sweden [51]; DSF, Gerber, Benteler, Menzel, Renotex, and Kleinewefers in Germany; M.T.R. (Matériel Textile du Rhône) in France; and Stork in Holland. Steam heating is used before batching, and the chamber is constructed of either pitch pine, polyester resin or stainless steel. Temperatures of 60–80°c. are used during storage, for times of up to 4–6 hr. This type of machine gives semi-continuous operation, and when several insulated storage chambers are available high production can be achieved. Further development of this pad–steam process by Benteler and by Smith has led to the design of fully continuous plants incorporating ingenious batching devices with double layers of cloth on two rolls. The Gminder belt-type conveyor for storage of the chlorite-impregnated cloth during steaming is constructed under licence by Farmer Norton Ltd. and provides an alternative method of treatment. A related conveyor system which consists of driven rollers is constructed by Benninger. Further machines have been introduced by Dungler in Switzerland; they use superheated steam at >105°c., which is blown at high velocity (25–30 metres/sec.) on to the cloth through nozzles in order to heat the acid chlorite-saturated material [52]. This process has been claimed to give much more rapid bleaching with sodium chlorite than is possible in other types of equipment, since hydrochloric acid-activation can be used, yet the chlorine dioxide formed does not cause corrosion as the

temperature is above 100°C. and all the metallic surfaces are dry. The heated cloth is stored for 10 min. at >100°C. in a small air-tight J-box lined with polytetrafluoroethylene, and then washed off.

Economic factors govern the type of process given in the different bleaching machines. In cotton bleaching a combination of mild alkali or solvent dewaxing and chlorite treatments will give excellent prepares for dyeing and printing, or good whites. Many variations are possible on linen cloth, depending on whether "green" or boiled yarn is to be processed and the weight-loss required [25]. The use of chlorite treatments, in conjunction with selected alkali steeps and treatment with alkaline peroxide and acid or alkaline hypochlorite, can reduce weight-loss to 10–15% and give good whites with minimum rise in fluidity.

Conclusions

The use of sodium chlorite as a bleaching agent for cellulosic fibres permits shorter processes, with lower weight-losses, direct bleaching of lignified impurities difficult to bleach by other methods, and minimum risk of chemical damage to the fibre. On the other hand chemical costs are high, and they may be accompanied by high overhead costs for the necessary machinery. Because of its relatively high cost, sodium chlorite must be used in the most efficient way possible, with minimum formation of chlorine dioxide and sodium chlorate and maximum decomposition of the agent itself.

Experimental

MATERIALS

Grey flax, in the form of 45s lea line yarn, was used. Commercial sodium chlorite (80%; Elektrochemische Werke München) was obtained from Charles Tennant & Co.

ANALYSIS OF SODIUM CHLORITE

Sodium Chloride

Mohr's method was used: 25 ml. of solution were brought to pH 7–8 before titrating with 0·1 N. silver nitrate.

Sodium Chlorite

To 10 ml. of solution were added 50 ml. of distilled water, 1 g. of potassium iodide and 15 ml. of 50% hydrochloric acid. This solution was then titrated with 0·1 N. sodium thiosulphate, and the results were calculated in terms of sodium chlorite concentration.

At pH values below 5 and at elevated temperatures, the amount of chlorine dioxide gas liberated becomes appreciable [53]. The solubility of this gas at elevated temperatures is not high, but it causes a small error in the figures given for chlorite concentration for pH values below 5, which are, nevertheless, some measure of the amount of bleaching capacity remaining in the solutions.

Sodium Chlorate

Total chloride was estimated and a correction was made for sodium chloride and sodium chlorite. To 25 ml. of the solution were added 50 ml. of distilled water and 10 ml. of 2 N. ammonium hydroxide. Sulphur dioxide was then passed through the solution for 2 min. After boiling for 5 min., 25 ml. of 2 N. sulphuric acid were added, and carbon dioxide was passed through the solution for 10 min. at the boil. One or two drops of 0·1 N. potassium permanganate were next added to destroy excess sulphur dioxide, and 6 g. of calcium carbonate to bring the pH to 8. Potassium chromate was then added as indicator, and the solution titrated with 0·1 N. silver nitrate [54].

BLEACHING PROCEDURE

The initial concentration of sodium chlorite was 5 g./litre in all experiments, and a constant liquor ratio of 20:1 was adopted. Clark–Lubs buffer solutions were used undiluted throughout, except for pH 2, when an extra 20 ml. of N-hydrochloric acid per litre were required to maintain pH 2 at 80°C. Experiments at 80°C. for 2 hr. were carried out with 20 g. yarn in a flask fitted with a mercury-seal stirrer and thermometer and placed in a water bath. Experiments at 96°C. for 2 hr. were carried out similarly in a boiling-water bath, whilst 121°C. was obtained by using a pressure cooker. In the latter case 10 g. samples of yarn were employed, and the solutions were placed in unstoppered 250-ml. Erlenmeyer flasks, which, after the level had been marked, were placed in the pressure vessel at 100°C. Twenty minutes were required to heat to 121°C., and this temperature was maintained for 90 min. Cooling to 100°C. required 10–15 min., after which the vessel was opened and the solutions immediately cooled to room temperature. The total time at >100°C. was 120–125 min. The yarn was cut into ½ in. lengths in all experiments, and washed, steeped in sodium bisulphite, neutralised, and rinsed before drying in air.

* * *

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COMMUNICATIONS

Relation of Apparent Diffusion Coefficient to the Time of Half-dyeing

W. F. KILBY

The relationship of the time of half-dyeing to the fractional exhaustion of a finite dyebath is considered in detail. The implications of these considerations for the theory and practice of dyeing are discussed with particular emphasis on dyeing from small volumes.

INTRODUCTION

The time taken by a dyeing system to attain an absorption of one-half of that at final equilibrium, $t_{\frac{1}{2}}$, is an easily determined experimental quantity which experience has shown, since its introduction [1, 2] some twenty-five years ago, is sufficient to characterise approximately the whole course of absorption in a particular dyeing system.

Vickerstaff [3] has noted that the theory of diffusion-controlled absorption from a finite dyebath, due to Wilson [4] and Crank [5], implies that, for a given dye, fibre, and temperature, the time of half-dyeing, $t_{\frac{1}{2}}$, should increase with a decrease in the fractional equilibrium exhaustion of the bath, ε, for example as a consequence of an increase in the ratio of the volume of the dye liquor to the volume of fibre present.

The purpose of the present paper is to establish the relationship of the time of half-dyeing to the fractional exhaustion in much greater detail than hitherto and to indicate briefly some of the implications of the new information for the theory and practice of dyeing.

THEORY OF ABSORPTION FROM A FINITE DYEBATH

The rate of absorption of dye by a fibrous mass immersed in a finite dyebath is complicated by the fact that the amount of dye present in the system is finite and that, as dye is absorbed by the fibre, the concentration of dye in the external solution decreases. The solution of the problem in a convenient form is due to Wilson [4].

For a cylinder sufficiently long that end-effects may be neglected (which is the case of most interest in the dyeing of textile fibres), and which is immersed in a dyebath of finite volume, with the assumptions (*a*) that there is efficient stirring in the bath so that the concentration of dye in the dye liquor may be assumed uniform throughout the bath, and (*b*) that the partition of dye at equilibrium between fibre and dye solution is constant and independent of concentration, Wilson [4] has shown that—

$$\frac{M_t}{M_\infty} = \frac{\varepsilon_t}{\varepsilon} = 1 - \sum_n \frac{4\alpha(1+\alpha)}{4+4\alpha+\alpha^2 q_n^2} \exp\left(-q_n^2 \frac{Kt}{a^2}\right) \qquad \text{(i)}$$

where—

M_t = Amount of dye taken up by the cylinder of radius a in time t
M_∞ = Amount of dye taken up at equilibrium
ε_t = Fractional exhaustion at time t, the fractional exhaustion being defined as the ratio of the difference between the initial and final concentration of the dye liquor to the initial concentration
ε = Fractional equilibrium exhaustion
α = A parameter related to ε by—

$$\left.\begin{aligned} \alpha &= \frac{1-\varepsilon}{\varepsilon} \\ \text{also } \alpha &= \frac{V}{(R+1)} \end{aligned}\right\} \qquad \text{(ii)}$$

where—

V = The ratio of the bath volume (ml.) to the dry weight of fibre (g.)

$R+1$ = Partition factor relating to the equilibrium partition between liquor and cylinder; the units will be ml./g.

R = Internal partition between the absorbed dye at a place and the mobile and unabsorbed dye in the same region; the q_n's are the non-zero roots of the equation—

$$\alpha q_n J_0(q_n) + 2 J_1(q_n) = 0 \qquad \text{(iii)}$$

$J_0(q_n)$ and $J_1(q_n)$ = The zero and first-order Bessel functions of the first kind respectively

K = Effective diffusion coefficient, and Kt/a^2 is a dimensionless quantity

The solution given by equation (i) is suitable for numerical computation only when Kt/a^2 is large; for small and intermediate values of Kt/a^2 it is very slowly convergent and quite inconvenient for numerical calculation. Crank [6] has developed alternative forms which are suitable for computation for small and intermediate values of Kt/a^2.

The most convenient of these solutions for the purpose of this paper is—

$$\frac{M_t}{M_\infty} = \frac{1+\alpha}{1+\frac{1}{4}\alpha}\left\{1-\exp\frac{4}{\alpha^2}\left(1+\frac{\alpha}{4}\right)^2\frac{Kt}{a^2}\ \operatorname{erfc}\left[\frac{2}{\alpha}\left(1+\frac{\alpha}{4}\right)\left(\frac{Kt}{a^2}\right)^{\frac{1}{2}}\right]\right\} \qquad \text{(iv)}$$

where the error function complement erfc x is defined by—

$$\begin{aligned}\operatorname{erfc} x &= \frac{2}{\pi^{\frac{1}{2}}}\int_x^\infty \exp(-\xi^2)\,d\xi \\ &= 1-\frac{2}{\pi^{\frac{1}{2}}}\int_0^x \exp(-\xi^2)\,d\xi \\ &= 1-\operatorname{erf} x\end{aligned}$$

where erf x denotes the error function.

TIME OF HALF-DYEING AND CALCULATION OF THE APPARENT DIFFUSION COEFFICIENT

Equations (i) and (iv) show that the ratio M_t/M_∞ (or $\varepsilon_t/\varepsilon$) depends only upon the dimensionless quantity Kt/a^2, and the parameter α. Curves showing the relationship between M_t/M_∞ and $(Kt/a^2)^{\frac{1}{2}}$ for a number of different values of $\alpha \geqslant 0{\cdot}10$ are given by Crank [6]. Here we are particularly concerned with the rate of dyeing when α may be considerably less than 0·1.

The time of half-dyeing, $t_{\frac{1}{2}}$, is that value of the time for which the ratio M_t/M_∞ is equal to 0·5; the dimensionless quantity $Kt_{\frac{1}{2}}/a^2$ is completely determined by α. It is convenient at this stage to introduce a special symbol, S_ε, to denote Kt/a^2.

The value of S_ε, corresponding to a specified value of α, may easily be calculated with the aid of equation (iv). A number of values for Kt/a^2 which are known by preliminary calculations to yield a value of M_t/M_∞ close to 0·5 are substituted into equation (iv), and the true value of S_ε may then be determined by graphical interpolation; such values are obtained with a precision of the order 1–2%. Values of erf x which are required may be obtained from published tables [7].

Values of S_ε for values of ε ranging from 0·30 to 0·999 are listed in Table I; an asterisk denotes that the calculation was carried out by the method described above. The remaining intermediate values were obtained by interpolation using, for this purpose, either the ratio S_ε/α for values of ε ranging from 0·30 to 0·89, or the ratio S_ε/α^2 for $\varepsilon \geqslant 0{\cdot}90$. The inaccuracy involved in the values obtained by interpolation is, in all cases, less than 2%. Smoothed values of S_ε/α and S_ε/α^2 are also listed in Table I. A plot of log $S_\varepsilon^{\frac{1}{2}}$ against log α is illustrated in Fig. 1.

If the equilibrium exhaustion, ε, and hence α, is known, Table I enables S_ε to be determined. A knowledge of the time of half-dyeing, $t_{\frac{1}{2}}$, and the effective radius, a, then permits the calculation of the apparent diffusion coefficient K.

S_ε varies rapidly with ε, particularly at high exhaustions, $\varepsilon > 0{\cdot}99$, and a small error in ε will be accompanied by a large error in the corresponding value of S_ε. Consequently an accurate determination of S_ε demands that ε should be determined with the greatest possible accuracy; certainly for $\varepsilon > 0{\cdot}99$ an accuracy of at least 10% in $(1-\varepsilon)$ is desirable. The most convenient and accurate method of determining the equilibrium exhaustion from experimental data involves the use of a plot of the dye taken up against the logarithm of the time. It is to be noted that an accurate determination of $t_{\frac{1}{2}}$ also depends upon the accuracy with which the equilibrium exhaustion is obtained. However, $t_{\frac{1}{2}}$ is not so sensitive to a small error in ε as is S_ε.

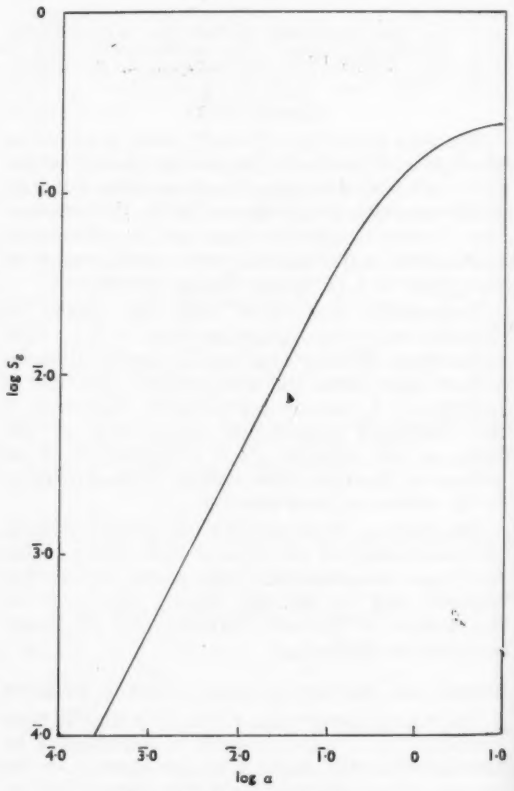

FIG. 1—Variation of log S_ε with log α

TABLE I

Numerical Values of S_ε, S_ε/α and S_ε/α^2

ε	α	$S_\varepsilon=\frac{Kt_{\frac{1}{2}}}{a^2}$	S_ε/α	S_ε/α^2	ε	α	$S_\varepsilon=\frac{Kt_{\frac{1}{2}}}{a^2}$	S_ε/α	S_ε/α^2
0	∞	$6{\cdot}32\times10^{-2}$	0	0	0·82	0·220	3·91	1·77	8·08
*0·30	2·333	3·66	$1{\cdot}57\times10^{-2}$	$6{\cdot}73\times10^{-3}$	0·83	0·205	3·51	1·71	8·36
*0·35	1·857	3·29	1·77	9·54	0·84	0·190	3·13	1·65	8·67
*0·40	1·500	2·93	1·95	$1{\cdot}30\times10^{-2}$	*0·85	0·177	2·81	1·59	8·98
*0·45	1·222	2·57	2·10	1·72	0·86	0·163	2·48	1·52	9·32
*0·50	1·000	2·21	2·21	2·21	0·87	0·149	2·14	1·44	9·64
0·51	0·961	2·14	2·23	2·32	0·88	0·136	1·85	1·36	$1{\cdot}00\times10^{-1}$
0·52	0·923	2·07	2·24	2·43	0·89	0·124	1·58	1·27	1·03
0·53	0·887	2·01	2·27	2·55	*0·90	0·111	1·31	1·18	1·06
0·54	0·852	1·94	2·28	2·67	0·905	0·105	1·19	1·14	1·08
*0·55	0·818	1·87	2·29	2·79	*0·910	0·0989	1·08	1·09	1·10
0·56	0·786	1·82	2·31	2·95	0·915	0·0929	$9{\cdot}67\times10^{-4}$	1·04	1·12
0·57	0·754	1·75	2·32	3·08	*0·920	0·0870	8·61	$9{\cdot}90\times10^{-3}$	1·11
0·58	0·724	1·69	2·33	3·22	0·925	0·0811	7·61	9·38	1·16
0·59	0·695	1·62	2·33	3·35	*0·930	0·0753	6·67	8·86	1·18
*0·60	0·667	1·56	2·34	3·51	0·935	0·0695	5·78	8·32	1·20
0·61	0·639	1·50	2·34	3·67	*0·940	0·0638	4·95	7·76	1·22
0·62	0·613	1·43	2·34	3·81	0·945	0·0582	4·19	7·20	1·24
0·63	0·587	1·37	2·34	3·98	*0·950	0·0526	3·48	6·61	1·26
0·64	0·563	1·31	2·32	4·13	0·955	0·0471	2·84	6·02	1·28
*0·65	0·538	1·24	2·31	4·28	*0·960	0·0417	2·26	5·42	1·30
0·66	0·515	1·18	2·30	4·45	0·965	0·0363	1·74	4·79	1·32
0·67	0·493	1·13	2·29	4·65	*0·970	0·0309	1·28	4·14	1·34
0·68	0·471	1·07	2·27	4·82	0·975	0·0256	$8{\cdot}91\times10^{-5}$	3·48	1·36
0·69	0·449	1·01	2·26	5·01	*0·980	0·0204	5·75	2·82	1·38
*0·70	0·429	$9{\cdot}61\times10^{-3}$	2·24	5·22	0·985	0·0152	3·25	2·14	1·41
0·71	0·408	9·01	2·21	5·41	*0·990	0·0101	1·46	1·44	1·43
0·72	0·389	8·54	2·19	5·64	*0·991	0·00908	1·18	1·30	1·43
0·73	0·370	8·02	2·17	5·86	*0·992	0·00807	$9{\cdot}36\times10^{-6}$	1·16	1·44
0·74	0·351	7·50	2·14	6·09	*0·993	0·00705	7·17	1·02	1·44
*0·75	0·333	7·03	2·11	6·34	*0·994	0·00604	5·28	$8{\cdot}74\times10^{-4}$	1·45
0·76	0·316	6·54	2·07	6·55	*0·995	0·00503	3·67	7·30	1·45
0·77	0·299	6·08	2·03	6·80	*0·996	0·00402	2·35	5·85	1·45
0·78	0·282	5·59	1·98	7·03	*0·997	0·00301	1·32	4·40	1·46
0·79	0·266	5·17	1·94	7·30	*0·998	0·00200	$5{\cdot}86\times10^{-7}$	2·93	1·47
*0·80	0·250	4·73	1·89	7·57	*0·999	0·00100	1·47	1·47	1·47
0·81	0·235	4·31	1·83	7·81					

More detailed information regarding methods for determining equilibrium exhaustion and time of half-dyeing is given by Vickerstaff[3].

When α is very small ($\alpha \ll 1$),

$$1+\alpha \simeq 1$$

and equation (iv) reduces to—

$$\frac{M_t}{M_\infty} \simeq 1-\exp\left(\frac{4}{\alpha^2}\,\frac{Kt}{a^2}\right) \operatorname{erfc} \frac{2}{\alpha}\left(\frac{Kt}{a^2}\right)^{\frac{1}{2}}$$

for $t=t_{\frac{1}{2}}$ we have, by definition—

$$\frac{M_t}{M_\infty} = 0{\cdot}5, \qquad S_\varepsilon = \frac{Kt_{\frac{1}{2}}}{a^2}$$

hence—

$$\frac{2}{\alpha} S_\varepsilon^{\frac{1}{2}} = \text{constant}$$

or

$$\log S_\varepsilon^{\frac{1}{2}} = \log \alpha + \text{constant} \qquad \text{(v)}$$

Thus for $\alpha \ll 1$, $\log S_\varepsilon^{\frac{1}{2}}$ varies linearly with $\log \alpha$ with a slope of unity. It is found empirically that for $\varepsilon > 0{\cdot}93$ the equation—

$$S_\varepsilon \simeq (0{\cdot}4380\varepsilon - 0{\cdot}2904)\alpha^2 \qquad \text{(vi)}$$

gives S_ε within 1% of the listed values.

Reference to Table I shows that the value S_ε/α varies slowly with ε between $\varepsilon=0{\cdot}30$ and $\varepsilon=0{\cdot}85$, reaching a flat maximum when $\varepsilon=0{\cdot}62$. The mean value of S_ε/α within this range is $2{\cdot}1\times10^{-2}$, and most of the individual values do not deviate from this mean by more than 20%; between $\varepsilon=0{\cdot}50$ and $\varepsilon=0{\cdot}70$, S_ε/α is constant to a first approximation.

ALTERNATIVE METHODS OF DETERMINING THE APPARENT DIFFUSION COEFFICIENT

The above treatment has been concerned with the determination of the apparent diffusion coefficient associated with a given dyeing system from the time of half-dyeing. However, the same data which are required for the determination of the time of half-dyeing and the equilibrium exhaustion may be treated in alternative ways to give values for the apparent diffusion coefficient, and these will be mentioned briefly for the sake of completeness.

It has been shown[6] that the limiting value of equation (iv) for small values of t is—

$$\frac{M_t}{M_\infty} = \frac{2}{\alpha}(1+\alpha)\frac{2}{\pi^{\frac{1}{2}}}\left(\frac{Kt}{a^2}\right)^{\frac{1}{2}} \qquad \text{(vii)}$$

so that a plot of M_t/M_∞ or $\varepsilon_t/\varepsilon$ against $(t)^{\frac{1}{2}}$ should be a straight line passing through the origin with a slope equal to—

$$\frac{4(1+\alpha)}{\alpha}\left(\frac{K}{\pi a^2}\right)^{\frac{1}{2}} = \frac{4}{(1-\varepsilon)}\left(\frac{K}{\pi a^2}\right)^{\frac{1}{2}}$$

and a knowledge of α or ε and a then permits the calculation of K. Again ε is required to be determined with a high degree of precision.

Equation (vii) may be written as—

$$\frac{M_t}{M_\infty} = \frac{4}{1-\varepsilon}\left(\frac{S_\varepsilon}{\pi}\,\frac{t}{t_{\frac{1}{4}}}\right)^{\frac{1}{2}}$$

Hence, if M_t/M_∞ is plotted against $(t/t_{\frac{1}{4}})^{\frac{1}{2}}$ the initial portion of the curve will have a slope—

$$\frac{4}{1-\varepsilon}\left(\frac{S_\varepsilon}{\pi}\right)^{\frac{1}{2}}$$

Calculated values of the initial slope, corresponding to a number of values of ε, are given in Table II.

TABLE II

Theoretical Values of the Initial Slope of M_t/M_∞ vs. $(t/t_{\frac{1}{4}})^{\frac{1}{2}}$ for Different Values of the Equilibrium Exhaustion, ε

ε	Theoretical Slope $\frac{4}{1-\varepsilon}\left(\frac{S_\varepsilon}{\pi}\right)^{\frac{1}{2}}$
0	0·57
0·30	0·62
0·40	0·64
0·50	0·67
0·60	0·70
0·70	0·74
0·80	0·78
0·90	0·82
0·95	0·84
0·99	0·86
0·999	0·87

Table II shows that the initial slope of the curve obtained by plotting M_t/M_∞ against $(t/t_{\frac{1}{4}})^{\frac{1}{2}}$ changes only slowly with the equilibrium exhaustion, particularly when $\varepsilon > 0{\cdot}90$.

Another method of treating the experimental data involves a plot of ψ against t where—

$$\psi = \frac{M_t}{M_\infty - M_t} \qquad \text{(viii)}$$

Fig. 2 shows calculated theoretical values of ψ plotted against Kt/a^2 for values of ε ranging from 0·3 to 0·9. In all cases the curves are sigmoidal in shape, but the intermediate portions of the curves are approximately linear over a fair range of t. The linear portion may be represented by the equation—

$$\psi = B\left(\frac{Kt}{a^2}\right) + C \qquad \text{(ix)}$$

where the parameters B and C depend only on the equilibrium exhaustion. Values of B and C obtained graphically from the theoretical plots are listed in Table III.

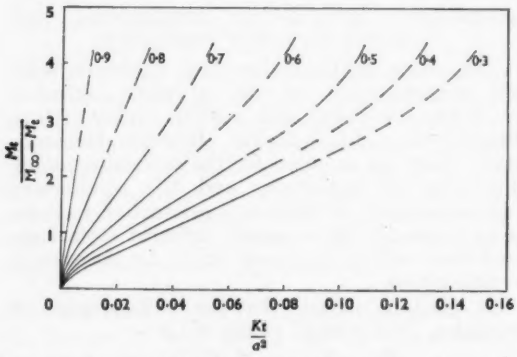

FIG. 2—Variation of $M_t/(M_\infty - M_t)$ with Kt/a^2 for values of ε ranging from 0·30 to 0·90

TABLE III

Variation of B and C with ε

ε	B	C
0	13·6	0·16
0·30	22·5	0·18
0·40	26·9	0·20
0·50	33·7	0·23
0·60	45·8	0·28
0·70	67·1	0·36
0·80	111	0·52
0·90	258	1·10

This method of presenting the data provides a further method of determining the apparent diffusion coefficient; if experimental values of ψ are plotted against t the slope of the linear portion is given by $B(K/a^2)$. The value of B, corresponding to a given value of ε, may be interpolated as in Table III and hence K may be calculated.

This method of treating experimental dyeing data is mentioned, since Vickerstaff[3] has found that the rate-of-dyeing curves for disperse dyes on nylon and cellulose acetate fibres, as well as direct dyes on cotton, may be approximately described by a hyperbolic relationship of the form—

$$\frac{1}{\varepsilon - \varepsilon_t} - \frac{1}{\varepsilon} = kt$$

where k is a velocity constant. This equation is equivalent to—

$$\frac{M_t}{M_\infty - M_t} = \varepsilon kt \qquad \text{(x)}$$

This relationship differs in form from equation (ix) only in that this equation contains an additional parameter. In dyeing experiments there is often a considerable scatter in the experimental results and, since small errors in M_t can have an appreciable effect on ψ, particularly near equilibrium, this could result in the drawing of a straight line through the origin when, in fact, it should theoretically make a small intercept on the ψ axis. The hyperbolic plot (equation (x)) is thus not greatly at variance with simple diffusion theory. The velocity constant, k, in equation (ix) may be interpreted in terms of the apparent diffusion coefficient and equilibrium exhaustion by approximating the slope of the two hyperbolic relations (equations (ix) and (x))—

$$k \sim \frac{B}{\varepsilon} \cdot \frac{K}{a^2} \qquad \text{(xi)}$$

APPLICATIONS AND IMPLICATIONS

With certain simplifying assumptions, Morton[8] has shown that the apparent diffusion coefficient, K, of the dye in the fibre during dyeing may be written—

$$K = \frac{3{\cdot}54(1+\varrho\sigma)fS_\varepsilon}{\varrho t_{\frac{1}{2}}} \times 10^{-7} \text{ cm}^2.\text{ sec.}^{-1} \quad \text{(xii)}$$

where—

- ϱ = Density (g./ml.) of dry fibre
- σ = Swelling (ml. H_2O/g. of fibre)
- f = Fibre denier
- $t_{\frac{1}{2}}$ = Time of half-dyeing (sec.) associated with a dyeing system of volume ratio V, and fractional equilibrium exhaustion, ε

here—

- V = Ratio of bath volume (ml.) to dry weight of fibre (g.)

Provided that the dyeing process is controlled by a simple diffusion process, the apparent diffusion coefficient may be calculated from dyeing data obtained in limited baths where ε is relatively high. The literature contains many series of results to which equation (xii) might be usefully applied.

In a given dyeing system where K is invariant, the time of half-dyeing, $t_{\frac{1}{2}}$, is proportional to S_ε. Reference to Table I indicates that S_ε decreases regularly and rapidly as ε approaches unity.

If ε is specified, then $t_{\frac{1}{2}}$ is inversely proportional to K; this provides the basis of the method of Boulton and Reading[2] for characterising the diffusion behaviour of direct dyes on viscose rayon in a dyeing system in which the salt content was adjusted to give $\varepsilon = 0{\cdot}50$.

Morton[8] has shown that if M is the diffusion coefficient of the mobile and unabsorbed dye molecules in the fibre, then the following relationship is approximately valid—

$$M = \frac{3{\cdot}54fVS_\varepsilon}{\alpha t_{\frac{1}{2}}} \times 10^{-7} \text{ cm}^2.\text{ sec.}^{-1} \quad \text{(xiii)}$$

This diffusion coefficient, which will be subsequently referred to as the mobility coefficient, is effectively the apparent diffusion coefficient, K, corrected for the substantivity of the dye, thus—

$$M = (R+1)K \quad \text{(xiv)}$$

where R is the internal partition coefficient, i.e. the ratio between dye absorbed at any place in the fibre and the concentration of mobile and unabsorbed dye at the same place.

The mobility, M, is taken to be a constant determined only by the nature of the fibre, the dye, and the temperature, but independent of the substantivity; every factor which tends to increase the substantivity will operate so as to decrease K proportionally.

Assuming that M is a constant independent of any variation in ε which may be caused, for example, by the addition of salt to a system consisting of cellulose and direct dye, then $t_{\frac{1}{2}}$ will be directly proportional to S_ε/α. It has been pointed out that the maximum variation of S_ε/α is within 20% when $0{\cdot}3 \leqslant \varepsilon \leqslant 0{\cdot}85$. For $\varepsilon > 0{\cdot}9$, S_ε/α decreases rapidly, but in this region S_ε/α^2 is approaching constancy.

The relative constancy of $t_{\frac{1}{2}}$ corresponding to medium values of ε, compared with its rapid diminution at high exhaustions, was an unexplained feature of early kinetic experiments[1] which now appears to be satisfactorily accounted for by equation (xiii).

One of the intentions of the present work is to provide a theoretical approach to the dyeing of woven fabrics from very small volumes, such as occurs in the jigger, on padding and in the Pad–Roll system. Here dye is absorbed from a system of small volume ratio which is assumed to be $V_2 \simeq 1$. The behaviour of a dye is usually characterised by a determination of the time of half-dyeing $(t_{\frac{1}{2}})_{V_1}$ from a 40–50 vol. liquor. It is required to compute approximately, $(t_{\frac{1}{2}})_{V_2}$ corresponding to the lower volume ratio V_2.

If the partition coefficient of dye between bath and fibre remains constant (as is approximately the case for a disperse dye on cellulose acetate, and for a direct dye used with a fixed proportion of salt on cellulose), then according to equation (ii) the change in exhaustion may be represented by—

$$\frac{V_1}{\alpha_1} = \frac{V_2}{\alpha_2} \quad \text{(xv)}$$

where α_1 and α_2 are derived from ε_1 and ε_2, the respective equilibrium exhaustions at volume ratios V_1 and V_2.

Again assuming the constancy of M, equation (xiii) implies that—

$$\frac{(t_{\frac{1}{2}})_{V_1}}{(t_{\frac{1}{2}})_{V_2}} = \frac{V_1 S_{\varepsilon_1}}{\alpha_1} \Big/ \frac{V_2 S_{\varepsilon_2}}{\alpha_2} = \frac{S_{\varepsilon_1}}{S_{\varepsilon_2}} \quad \text{(xvi)}$$

because of equation (xv). If $\varepsilon > 0{\cdot}75$ (as is usually the case) then S_ε is, to a first approximation, proportional to α^2 and equation (xvi) becomes—

$$\frac{(t_{\frac{1}{2}})_{V_1}}{(t_{\frac{1}{2}})_{V_2}} = \frac{\alpha_1^2}{\alpha_2^2} = \frac{V_1^2}{V_2^2} \quad \text{(xvii)}$$

The approximation involved in deriving equation (xvii) may lead to an under-estimation of $(t_{\frac{1}{2}})_{V_2}$ by a factor of 2. This, however, is negligible, as is shown later. Equation (xvii) gives the expectation of $t_{\frac{1}{2}} = 0{\cdot}2$ sec. in 1 vol. for a medium-slow dye having $t_{\frac{1}{2}} = 300$ sec. in 40 vol. The calculated speed of absorption in 1 vol. is much higher than hitherto anticipated; the potential speed of dyeing is so great that the rate-controlling process is likely to be the relative motion of the fibre and the interstitial liquor rather than the diffusion of the dye into the fibre.

Absorption of dye is almost complete within a period of $20t_{\frac{1}{2}}$, so that most dyes should, under optimum conditions, be fixed from a 1 vol. dyebath within a few seconds. At this stage the fibres will be ring-dyed and diffusion to the centre of the fibres will take a much longer period. However, the mere fixation of dye has important technical implications which deserve closer attention. It has been possible, for example, to treat successfully the theory of jigger dyeing by methods based on the present considerations.

The practical utility of equations (xii) and (xiii) with dyeing systems of high equilibrium exhaustion has been demonstrated by remarkable regularities observed in the mobility coefficient, M, so calculated for a series of disperse dyes on secondary cellulose acetate fibres. It must be emphasised once again that a condition for success is a very accurate determination of ε, particularly when $\varepsilon > 0{\cdot}90$.

CONCLUSIONS

Provided that the absorption of dye by fibre can be represented as being controlled by a simple diffusion process, the time of half-dyeing and the equilibrium exhaustion are sufficient to characterise the course of dyeing. An extensive table is presented giving values of S_ε for a wide range of values of the fractional equilibrium exhaustion ε.

Alternative methods of treating experimental dyeing data are discussed and it is noted that a hyperbolic relationship of the form—

$$\psi = \frac{M_t}{M_\infty - M_t} = \varepsilon k t$$

is not inconsistent with the theoretical relationships expected for dyeing from a finite volume. It is suggested that the velocity constant, k, may be interpreted in terms of the apparent diffusion coefficient and a function of the equilibrium exhaustion which is tabulated.

The application and implication of the theory are discussed particularly with reference to dyeing from small volumes, where it would seem that fixation of dye should take place much more rapidly than previously anticipated. In this respect the present work should provide a basis for further experimental investigation.

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The Effect of Environment and Substituents on the Photochemical Activity of Anthraquinonoid Vat Dyes and the Rôle of n-π^* Transitions

N. K. BRIDGE

The well-established correlations between dye fading and the phototendering caused by vat dyes on the one hand and dye affinity, aggregation, radical stability, electromeric effects, etc., on the other, are reviewed. Recent work, including flash spectroscopy, photolysis of model systems, studies of fluorescence and absorption spectroscopy, and studies indicating the existence of both singlet and triplet n–π^* transitions, is discussed, and this leads to the suggestion that n–π^* transitions are of fundamental importance. Evidence is collected to substantiate this. Factors which may affect the transition, especially hydrogen bonds involving the n-electrons and electromeric effects, are considered, as well as processes influencing the singlet–triplet ratio. It is shown, in terms of the relative amounts of singlet and triplet formed, how the observed difference between the efficient cyclic process of photosensitisers can be explained. Finally, these arguments are applied to a few well-known regularities of commercial dyes.

INTRODUCTION

The fading and phototendering caused by vat dyes has been the subject of a great deal of research since it was found that these compounds often react readily with fabrics on exposure to light [1, 2]. This paper is an attempt to summarise briefly the main correlations which have been obtained between their photochemical activity and various factors, as well as to review in more detail some recent results which have given a clearer insight into the underlying processes and to indicate how these results, in particular those concerning the electronic energy levels involved, lead to a new interpretation of the variations in activity of dyes under different conditions and suggest new lines along which the final answer may lie. The main points to be discussed are the identity and importance of the primary light-absorbing act, and not the subsequent chemical reactions.

Several regularities have been observed, but only a few have received any explanation, and this category will be considered first. Increased affinity of the leuco dye for the substrate is accepted as an important factor "enabling the carrier action of the dye to be exercised more effectively" [3] and eading to higher activity. Several authors have considered this [4–6], and the various factors affecting dye substantivity have also received detailed attention [7]. Recently Oster *et al.*[8, 9] have shown how the presence of polymeric materials in solution markedly increases the fading of basic dyes.

A factor which is to be distinguished from this affinity effect is the actual physical state of the dye, in particular the amount of crystallinity and aggregation. The process of soaping or steaming vat dyes leads to increased crystal size and aggregation, and this in turn has been shown to correspond to increased optical density of the dye before exposure and, sometimes, to increased fastness [4, 5, 10], both of which are desirable effects. Waters *et al.*[10] explained the increased absorption on the basis of perturbation of the dye energy levels resulting in more intense but lower wavelength transitions. Moran and Stonehill [11] have recently shown that there is very little, if any, such wavelength shift, but that the dye fluorescence decreases markedly, thus leading to an apparent optical density increase. The latter authors also point out (p. 793) that such crystalline dyes are semiconducting in light, and that this could lead to energy transfer throughout the crystal, much as is at present supposed to occur in the chromophores

of photosynthesising cells [12]. This idea that energy transfer throughout aggregates of dye molecules might occur was earlier suggested by Schiebe [13] for cyanine dyes to explain the quenching of their fluorescence. More recently, Sheppard [14] has modified Schiebe's ideas and indicated that water molecules between each dye molecule are probably important in facilitating such transfer. It seems likely that these water molecules would be hydrogen-bonded to the dye and so facilitate the transfer of energy; the recent work of Reid and Connor [15] demonstrates the possibilities of such energy transfer through hydrogen bonds. However, if the movement of electronic energy through the crystal is of importance, the energy is probably dissipated through coupling with crystal lattice vibrations, rather than concentrated at a substrate bond, in view of the *decreased* fading and tendering of the material caused by vat dyes on crystallisation. Baxter *et al.*[16], in a recent study, have confirmed the widespread aggregation of dyes, but consider that the lower activity is due to a smaller dye–air interface.

Venkataraman [17] has suggested that the stability of the intermediate radical presumably formed on exposing quinones to light, viz. the semiquinone radical, will be a measure of the dye's sensitising power, and he cited evidence in support of this view. Recently Bridge and Porter [18], and Bridge and Maclean [19], have found that these semiquinone radicals are present and stable when formed in deoxygenated irradiated solutions. However, it is not obvious why such stability (observed in the absence of oxygen) should confer activity on a dye, and in fact recent observations (see ref. 20) have indicated that in the *presence* of oxygen the stability is reversed and the poor-sensitiser semiquinone radical is more stable towards oxygen.

Another group of regularities has been observed but not satisfactorily explained; perhaps the most widely quoted is that yellow and orange vat dyes are generally the most active. Related to this is the bathochromatic shift (in the visible) which parallels reduced activity [5], and also the strong absorption in the 360–400 mμ. region which, as Scholefield and Turner [21] have pointed out, leads to activity. Of great importance is the effect of basicity of substituents, which has been considered by many workers, especially Kunz [22] (see also Venkataraman [23] and Landolt [24]). It has been found that negative (basic electron-donor) substituents usually reduce the activity, even though they increase the solubility of the leuco form.

Attempts have been made to correlate light fastness with tendering ability (see e.g. ref. 5, p. 529). However, it should be borne in mind that fading which is apparent as a change or loss of visible colour is not necessarily a good, quantitative test of the relative amounts of chemical change occurring in different dyes. Two other regularities observed are that substitution in the 2-position of an anthraquinonoid dye leads to greater tendering than substitution in the 1-position, and that unsubstituted quinones, e.g. anthraquinones [3], naphthaquinones, dibenzpyrenequinones and pyranthrone (Fox [5]), have definite activity, the least complex being the least active.

Lastly it has been observed that certain substituents affect the activity in a definite manner, but there are so many different substituents that it is not profitable to list them all. One or two, e.g. sulphurised substituents (Venkataraman [1], and Fox [5]), nearly always promote reactivity— the worst dye known, Cibanone Yellow R, is an example— and a few, such as the acridones [1], are not active. Halogens affect the reactivity in either sense [1, 5, 25]; methyl and hydroxyl groups also change the activity. More clear-cut substituent effects have been found for anthraquinone itself, but these will be referred to later.

RECENT ADVANCES

It is obvious from the above that there can be no single explanation of fading and tendering and that the answer probably lies in a combination of many factors. So far the following factors have been mentioned: basicity of the substituents, bonding to the substrate (H-bonding), the colour, and the state of the dye. These, even taken together, do not provide anything like a full explanation of the observations. However, the following more recent experiments have led to a clearer understanding of the various processes and have disclosed additional factors which should help towards a better understanding of the problem.

For vat dyes, the "model system" technique, used by Bolland and Cooper [26] in the photosensitised oxidation of ethanol by anthraquinones, showed accurately that the primary process following light absorption is reaction of the excited state with the substrate ethanol to form a semiquinone radical, subsequent reactions with oxygen and the substrate leading to the observed oxidative degradation of the alcohol. Later, Cooper [27] found that substituted anthraquinones can be divided broadly into sensitisers and non-sensitisers for this process. In the former group were the sodium salts of the 2-sulphonic and 2,6- and 2,7-disulphonic acids, and the 2-methyl and 1- and 2-chloro derivatives. In the latter group were the sodium salts of the 1-sulphonic and 1,5- and 1,8-disulphonic acids, as well as all hydroxy and all amino-anthraquinones. Wells [28] later showed that this primary process was one of hydrogen abstraction and not electron transfer. Applying the technique of flash photolysis, Bridge and Porter [18] demonstrated the existence of the proposed semiquinones, as well as the triplet state of the dye. In the case of the simple tetramethyl-*p*-benzoquinone (duroquinone)— a poor sensitiser— it was shown that the excited singlet state (Q*), and not the triplet (T), reacts with the substrate liquid paraffin (RH) to form the above semiquinone radical (QH·), and that, in ethanol, hydrogen abstraction is the primary act—

$$Q + \text{Light} \rightarrow Q^* \rightarrow Q \qquad \text{(i)}$$

$$Q^* \rightarrow T \rightarrow Q \qquad \text{(ii)}$$

$$Q^* + RH \rightarrow QH\cdot + R\cdot \qquad \text{(iii)}$$

The formation of the above radicals has since been studied by Bridge and Maclean [19] for commercial vat dyes in deoxygenated solutions, and their

general behaviour has been shown to be similar to the above.

The recent series of papers by Moran and Stonehill already referred to [11] has underlined the difficulty facing any attempt at complete explanation of the problem. These authors showed that there is little correlation between activity and absorption in the visible region of the spectrum. However, they pointed out that all the active vat dyes studied had a weak absorption in the 400 mμ. region which they attributed to a "forbidden" singlet–triplet transition, and that no inactive dye had such an absorption (although they say that it could easily have been missed). It is nevertheless important to note that this observation is not general, since there is sometimes very little difference in spectrum between active and inactive dyes of the same colour. Evidence was also presented that the visible absorption of substituted anthraquinones is mainly due to the "x band"[29], i.e. to a transition involving a dipole-moment change in the long axis (x) direction of the molecule, this band being bathochromically shifted from the near ultraviolet by the electromeric effects of substituents. They stressed that visual or even simple spectrophotometric examination of an exposed dye is not as good a test of fading or tendering ability as are the fluorescent changes. This serves to emphasise a further difficulty previously noted, viz. that small changes in visible colour do not necessarily imply small amounts of chemical change, since the visible colour is so sensitive to the precise shape of the absorption and fluorescent band that a complete spectrum should be obtained before drawing final conclusions.

The question of the electronic transitions involved in quinone photolysis is of the utmost importance, and it is necessary to consider the possibilities in some detail. For simple quinones there are two main types of transition responsible for the ultraviolet and (weak) visible spectrum [29–33], viz. (1) the π–π^* transition involving excitation of a non-localised π electron to an antibonding π^* molecular orbital and effective cancelling out of the bonding of one other π electron (the x and y bands of Lewis; the K bands of Burawoy), and (2) the weak n–π^* transition in which a non-bonding (n) electron, from the lone pairs localised on the oxygen atom, is excited also into an antibonding π^* molecular orbital (the y or z band of Lewis and the R band of Burawoy). Both transitions can lead to either a singlet or to a triplet excited state, but the singlet–triplet crossover is "forbidden" by selection rules (conservation of spin); in addition the singlet–singlet n–π^* transition is formally "forbidden" by symmetry (no overlap of ground and excited state orbitals). Consequently the observed intensity of the n–π^* transition must be due to some local perturbation (vibrational or spin-orbit) which makes it partially "allowed". (The exact nature of the perturbation is not clear, see e.g. $H_2C{=}O$ [34].) Fig. 1 illustrates the change in electron distribution and energy levels for the n–π^* transition.

It should be noted that, for quinones, the excited singlet–triplet crossover is relatively frequent [35].

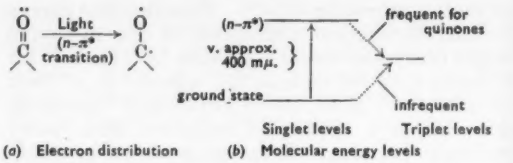

FIG. 1— Electron Distribution and Energy Levels associated with the n–π^* Transition in Quinones

A further important point concerns the chemical reactivity of an excited singlet compared with a triplet state. It will be recalled that the work of Bridge and Porter [18], already outlined, showed that for duroquinone, contrary to previous expectation, the triplet state does not react with the substrate, but probably the singlet is responsible. Abrahamson has recently confirmed this observation for other quinones [36]. However, there is really no *a priori* reason why the triplet state should be more reactive than the singlet, since electronically they are identical, apart from spin direction, and any difference that does appear is probably due to the longer life of the metastable triplet state (approx. 10^4 times longer than that of the singlet), to its slightly lower energy, or to some factor involving spin–spin interaction. One example of the latter would be reaction with oxygen in its ground ($3\Sigma_g^-$) triplet state.

STRUCTURE AND PHOTOCHEMICAL ACTIVITY

In the case of quinones, the photochemical reaction discussed above is initiated at the carbonyl oxygen, the dye molecule being excited by light and then abstracting a hydrogen atom from the substrate (see equation (iii)). If this is the underlying process in the fading and phototendering caused by this type of molecule, then a study of the electronic configuration in this region, before and during light absorption, should be profitable.

Before light absorption, there is good evidence that the quinone oxygen can be hydrogen-bonded to the substrate, the previously discussed n-electron presumably being involved. In solution, experiments on the ultraviolet blue shift of the n–π^* transition, as well as infrared studies, indicate this [37]. Venkataraman [38], and Peters and Sumner [7], have discussed hydrogen bonding of vat dyes in the solid (cellulose) polymers. In view of this bonding the n–π^* transition must be of the greatest importance, since it involves the excitation of one of the (n) electrons actually taking part in this hydrogen bond; consequently any factor which influences the transition will probably alter the photochemical reactivity.

The evidence that this weak, long-wavelength transition is photochemically active is as follows. Egerton [39] found that the rate of degradation of textile fibres by near ultraviolet and visible light in the absence of dyes is slow, but that the short wavelengths are much more active. Vat dyeing was found actually to *desensitise* the fibres to this short wavelength degradation, whereas they became more sensitive to the longer wavelengths (near ultraviolet and visible). Moran and Stonehill [11] found that tendering was more nearly correlated with weak absorption in the 350–400 mμ. region

than with the far ultraviolet strong absorption. That a weak transition is probably active is implied by the observation of several authors (especially clearly demonstrated by Cooper for simple anthraquinones and derivatives already referred to [27]) that there is sometimes very little difference between the spectra of active and inactive dyes. The low quantum yields (ca. 10^{-5}, [4, 40]) found may be due to a very small part (n–π^*) of the observed light absorption being active in photolysis, the rest being used up in an overlying but less active (π–π^*) transition. (Alternatively, since the quantum yield is usually observed to be smaller for a larger molecule— other factors being equal [4]— the dissipation of absorbed light energy by internal rearrangement might be an important factor.) Recently, direct evidence for the reactivity of the n–π^* transition has been obtained using the flash spectroscopy technique [20], by varying the wavelength of the flash and observing the quantum yield of radicals and triplet state.

If these n–π^* transitions are important, it is interesting to inquire what might be expected to influence them and so alter the photochemical reactivity. Clearly, in order to answer this question in detail, a thorough study of the position of the singlet and triplet energy levels, as well as of the factors influencing the various transitions, would have to be undertaken. Qualitatively, however, the following would be expected to have an effect. Firstly a hydrogen bond involving the carbonyl oxygen, or the binding of a proton to it, e.g. under acid conditions [41, 42], would render the excitation of the n-electrons more difficult and lead to reduced photochemical activity. Any substituent which interfered with the formation of such bonds could modify the transition; for example OH, by forming intramolecular hydrogen bonds with the carbonyl group, would wholly or partially prevent solvent H-bonding or give rise to new resonance possibilities and hence new transitions [43] at the expense of the n–π^* transition.

The important electromeric effect of substituents has already been stressed. Spectroscopically it is well established that the wavelength and sometimes the intensity of n–π^* transitions (R bands) are very sensitive to such effects [31, 33, 44, 45]; the (weak) electron-attractors have much less effect than the (strong) electron-donors. This is because the n–π^* transition corresponds to the movement of electrons away from the carbonyl oxygen and towards the carbon, whereas donating electrons to the carbon ring, and so to the oxygen, opposes this, resulting in a higher transition energy and the observed blue shift. Simultaneously, the electron-donors, by making the oxygen more negative, increase the strength of the H-bond, resulting in more difficult n-electron excitation; however, the extent to which these two effects are separable is debatable. In addition, it is observed that the intense π–π^* transition also moves to longer wavelengths, thus further obscuring the weak n–π^* as it moves to shorter ones; consequently, if the latter is the reactive transition, the photochemical reactivity will be reduced— in general agreement with observation [22, 23, 24]. Thus, the simple anthraquinones substituted by the strong donors NH_2 and OH are non-sensitisers for the photosensitised oxidation of alcohol [27], although it should be noted that exceptions to this observation are to be found amongst the simple disperse dyes, e.g. Duranol Orange G (C.I. Disperse Orange 11). An additional factor might be that a red shift enables more of the higher vibrational levels of the upper state to be activated by light absorption, so that more activation energy is available for the formation of the semiquinone radical by hydrogen abstraction.

In addition to the effects on n–π^* transitions as a whole, there is the more detailed question of the effects on the "forbidden" singlet–triplet transition already discussed. Several factors are known to influence such intercombinations [46], of which one of the most important for the purposes of the present discussion is the proximity of the n-electron to the nucleus of the heaviest atom in the system. Heavy atoms (O in this case) as well as tight binding of the electron will enhance the S→T at the expense of the S→S transition. A second factor is the near presence of strongly paramagnetic atoms which facilitate such "forbidden" transitions [44] by the magnetic, perturbing effect of their unpaired electrons. However, in order to correlate activity with such effects as these, it is necessary to decide whether the singlet or the triplet state is the reactive one in any particular case. It has been noted that for quinones there is some evidence that the singlet state is more reactive, and assuming for the moment that this is general (although there are no real grounds for so doing), then electron-attracting substituents for example should, by withdrawing the n-electrons nearer to the (heaviest atom) oxygen nucleus, promote the S→T conversion and so reduce tendering, contrary to observations. Such a correlation might prove feasible when further information is obtained concerning the particular reactive state.

However, the empirical observation that lakes— which are metal chelates consisting of a dye as ligand co-ordinately bonded (*via* the n-electrons) to a metal ion— are in general very fast to light [47, 48] lends some support to the theory that the triplet state is not reactive, since here the perturbing metal ions are very well placed to promote S→T transitions. Also, the recent observation of McRae and Kasha [49] that aggregation increases the phosphorescence of dyes, and their explanation of this as increased probability of singlet–triplet internal conversion, leads one to expect decreased photochemical activity on aggregation if the triplet is not reactive, as is observed.

APPLICATIONS TO SENSITISERS AND DYES

The above considerations may be used to explain many phenomena in the field of dye photochemistry. Of great interest is the varying sensitising power of simple anthraquinones. Cooper [27] found that some of these, as well as other carbonyl compounds, could very efficiently sensitise the photochemical oxidation of alcohols by a cyclic mechanism, whilst others could not. For the poor

sensitisers the reaction was found to be strongly inhibited by oxygen[50, 51]. In addition, Schenk and Koltzenberg[51] have used these non-sensitisers, e.g. naphthoquinone and hydroxy- and amino-anthraquinones, to promote an alternative, presumably non-cyclic and relatively inefficient oxidation of a substrate such as an α-terpene, in which oxygen is "transmitted" to the terpene with resulting ascaridol formation. On the other hand the sensitisers act by direct reaction of the excited state, *not with oxygen* (Cooper[27] and Wells[52]) but with the substrate ethanol, to form a semiquinone radical, followed by a very efficient cyclic photo-oxidation of the substrate.

These results can be interpreted in the light of the above discussion if it is assumed that the excited singlet reacts with the substrate, and that poor sensitisers pass more readily into the triplet state and also react with oxygen faster than does the sensitiser. Possibly the magnetic perturbation of the (paramagnetic) oxygen enhances the singlet–triplet crossover in this case. Additional flash-photolysis information on this point has recently been obtained[20], and it has been found that poor sensitisers react before radical formation with any oxygen present (and that the radicals subsequently formed react only slightly with the O_2), but sensitisers do *not* react with O_2 before radical formation, and yet the lifetime of such radicals is markedly reduced by it.

Consider now the application of the above ideas to simple anthraquinone sensitisers and to commercial dyes. The tendering yellow and orange vat dyes absorb in the blue at approximately 400–450 mμ., which is in the expected region of the active n–π^* transitions, whereas the other (usually strong) visible colours probably do not correspond to bathochromically shifted n–π^* transitions (since such shifts usually reduce the intensity), but to entirely new and less active transitions.

Substitution in the 2-position of simple anthraquinones usually leads to greater reactivity than that of the 1-substituted compounds. This is in line with the known effects on the n–π^* ("quinonoid") transitions[43, 44, 53], which could be due either to direct electromeric effects or to the steric effects of large groups in the 1-position interfering also with the n-electron bonding to the substrate. For example, SO_3^- and Cl belong to the weak-activating, electron-attracting group, yet only SO_3^- in the 1-position is a non-sensitiser. The fact that sulphur dyes (like the very bad Cibanone Yellow R which contains the sulphinyl group) are so reactive, is probably due not so much to any electromeric effects (since S is electron-donating), but to the ease with which their non-bonding electrons can be excited[44], leading perhaps to direct reaction with the substrate at the vacated sulphur non-bonding orbital— similar to the reaction at the carbonyl oxygen.

As regards halogen substitution, in addition to weak electromeric tendencies, the heavier Br atom would be expected to promote the S→T transition and so, if T is not reactive, reduce the tendering activity. That this can occur is shown by the tendering activity results tabulated by Egerton[54], and by Bamford and Dewar[4]. Cibanone Golden Yellows GK (C.I. Vat Yellow 4) and RK (C.I. Vat Orange 1) are the same, except that the latter has a single Br replacing a H atom; the former has a higher tendering activity than the latter. The same applies to dyes of the pyranthrone series, viz. Caledon Gold Orange G (C.I. Vat Orange 9); Cibanone Golden Orange 2R (C.I. Vat Orange 2); Caledon Orange 2RT (C.I. Vat Orange 2); and Caledon Brilliant Orange 4 or 6R (C.I. Vat Oranges 4 and 3), where hydrogen atoms are replaced by one, two, or three bromine atoms respectively and the activity gradually decreases. Also in the above tables is to be found a very clear-cut example of the great reduction in tendering activity expected when the chlorine atom of Cibanone Yellow 2GR (C.I. Vat Yellow 24) is replaced by an amino group to form Cibanone Red G (C.I. Vat Red 28).

SUMMARY AND CONCLUSIONS

The fading and phototendering induced by vat dyes have previously been correlated with—

(1) The affinity of the leuco dye for the substrate, leading to higher activity

(2) The physical state of the crystalline dye aggregate; more crystallinity corresponding to less fading

(3) Various regions of the spectrum, both emission and absorption, of the dye

(4) The nature and stability of the radicals produced on irradiation; greater reactivity being assumed for more stable radicals

(5) Basicity of substituents and their position in the molecule; electron-donors broadly speaking reducing the activity

(6) Miscellaneous activating and deactivating groups.

Almost certainly all of these factors do influence the activity of any one dye on any given material, but in addition it is proposed that the following may be included among the underlying causes of the above correlations, or even be additional factors—

(*a*) The excitation of non-bonding electrons to antibonding π^* molecular orbitals (n–π^* transitions)

(*b*) The H-bond involving the above n-electrons on the oxygen atoms

(*c*) Factors influencing the n–π^* transition, e.g. electromeric effects

(*d*) The position and ratio of S to T excitation of the n–π^* and π–π^* transitions and factors influencing them, e.g. paramagnetic ions.

There are many possible ways in which the ideas expressed above could be confirmed and expanded. A detailed study of the weak "forbidden" n–π^* transitions of dyes, whether by emission or absorption spectroscopy at various temperatures and in various solvents, might be fruitful, although some observations will no doubt be frustrated by the other stronger and overlapping transitions. It would be interesting and profitable to study other

classes of dyes containing a hetero atom, e.g. dyes of the azo, nitroso, triphenylmethane, or indigoid type. Of great importance would be the direct observation that other molecules react *via* the singlet rather than the triplet state. For this purpose flash spectrophotometry of rigid glasses would probably be necessary. Theoretical studies of the singlet and triplet energy levels will probably prove in the end to be the most profitable. The effect of additives, e.g. both paramagnetic and heavy atoms, on the S→T conversion process is being actively studied in a number of laboratories. So far [20] it has been found that, in the case of a simple anthraquinone sensitiser in alcohol, there is no detailed relation between radical production as detected by flash spectrophotometry and paramagnetism or molecular weight of added ions, although the complexity of the system is such that it is difficult to be certain of the species present.

In conclusion, it has become increasingly clear to workers in this field that there is no single comprehensive answer to the tendering problem. New ideas of molecular structure and reaction mechanisms, as well as advances in spectroscopy, seem to suggest even more factors on which the reactivity of a molecule may depend. However, it now seems reasonably certain that, as soon as a full knowledge of the electronic transitions and of the immediate primary products is obtained, then a final answer will not be far away.

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* * *

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Dyeing Education in Glasgow

From Anderson's University (1796) to the Royal College of Science and Technology (1958)

R. A. PEEL

The jubilee of the opening of the colour chemistry and dyeing laboratories in the college now known as The Royal College of Science and Technology, Glasgow, is commemorated by an account of the struggle for their establishment. The history of the college, which includes a strange incident in the career of W. H. Perkin, is surveyed. It is suggested that the Glasgow area is ideal for dyeing and textile manufacture, and that education in dyeing is a first priority.

ANDERSON'S UNIVERSITY

It is a little over 50 years since courses in dyeing were established as a part of the applied chemistry curriculum of the college now known as The Royal College of Science and Technology, Glasgow. This is a suitable moment to recall the history of those 50 years and to remember that, 150 years ago, the mechanics and manufacturers of Glasgow had so increased their skill and knowledge by education that their labours were a pattern for the world and their manufactures were exported all over it. How did this education begin? How did it lead to the Mechanics' Institutes, those forerunners of technical education in the great industrial centres of Great Britain?

John Anderson, M.A., F.R.S.E., F.R.S. (see Fig. 1), the founder of the college, was Professor of Natural Philosophy in the University of Glasgow during the years 1757–96[1]. He was born in the year 1726, son and grandson of Presbyterian ministers, remained unmarried, and was pugnacious and disputatious with his colleagues (amongst whom was Adam Smith, author of *The Wealth of Nations*). Yet he was a popular lecturer with his students, widely respected by the Glasgow citizenry, and known abroad for his invention and practical acumen. He organised courses of lectures in the University suitable for mechanics and artisans, who received popular lectures in physics and were admitted as "anti-toga", i.e. they did not wear the red gown of a University student. He published in 1786 for the benefit of those attending his "anti-toga" class ("town's people of almost every rank, age, and employment") his *Institutes of Physics*, which was so successful that it ran to five editions, the last being published in 1795. He visited the artisans at their daily work, and taught them at his classes to understand more clearly what they were doing and the underlying scientific principles. He bequeathed in his famous last will and testament all his property "except what is contained in the painted chest with three locks, . . . to the founding of an Institution for the Public Good and the Improvement of Science, to be known as Anderson's University." The will expressed very clearly Anderson's feelings about his *Alma Mater*, besides giving explicit instructions for the formation of the new body. He gave, by inference, his opinion of his old colleagues when he wrote: "No person connected with the University of Glasgow . . . can be connected with Anderson's University . . . The professors of Anderson's University shall not be permitted, as in some Colleges, to be Drones and Triflers, Drunkards . . ." He was an early advocate of joint education, and planned in his will a "Ladies' Course", "so that Glasgow ladies shall be the most accomplished in Europe".

Although Anderson left no funds to carry out his intentions— indeed after settlement of his debts there was a debit balance of £55— his trustees were determined that they should be fulfilled. This college bears the distinction, probably unique, of having been founded on a deficit. His valuable library and unique scientific apparatus were a nucleus around which his trustees could build, and in the year of his death the new "University" was started (named "Anderson's Institution" until 1828, when it became "Anderson's University"). The records of the first session include references to practical experiments in bleaching, dyeing, calico printing, etching, and engraving, amongst a large number of subjects demonstrated. "The chief design of this Institution", according to an advertisement[2] drawn up by Dr. T. Garnett, Professor of Natural Philosophy in the new Institution, was "to afford young Gentlemen intended for the Arts, Manufactures or Commerce, an opportunity of acquiring such a portion of useful knowledge as will qualify them for the society to which their fortunes insure them admission, which will throw light on the different processes of the Arts, and enable them to bring them to perfection; or which will serve to sooth and fill up in a rational and profitable manner those hours which everyone must find unemployed in business. Considered in this light it may form a valuable appendage to the College and University of Glasgow, and enable this City to furnish a more complete Course of useful Education than any other place in Britain." The "Mechanics' class" flourished: in 1806 it attracted 500 manufacturer and operative artisans and was approved by the Government; in 1823 it seceded to form the Glasgow Mechanics' Institution, the exemplar of similar institutions throughout these islands.

W. H. Perkin and Anderson's University

A succession of distinguished Professors of Natural Philosophy, including Drs. G. Birkbeck and A. Ure, influenced the early teaching of applied science in this university. When Dr. Ure resigned in 1830, Chemistry became a separate Chair. The holder of this Chair from 1839 to 1870 was Frederick Penny (see Fig. 2), a popular lecturer who had a wealthy consulting practice as a main source of income. In 1869, James Young, LL.D.,

F.R.S., of Kelly and Durris, the founder of the Scottish shale-oil industry, and President of Anderson's University (1868–77) offered 10,000 guineas to found the "Young" Chair of Technical Chemistry, the first Chair of Applied Chemistry in Britain[3]. The first appointment was offered in September 1869 to W. H. Perkin, the "father" of dye chemistry, then aged 31 (see Fig. 3 and 4). Penny was resentful of the proposed appointment, news of which was published in the *Glasgow Herald* (7th Sept. 1869), and wrote Perkin a letter of protest (Fig. 5). Perkin was upset, sent Penny's letter to his Glasgow friend Robert Hogg (of Henderson & Hogg, chemical merchants) (see Fig. 6) and did not take up the appointment. There is a fine portrait (presented by Robert Hogg) of Sir W. H. Perkin in the College, labelled "Young Professor of Technical Chemistry 1870–1". The College *Calendar* similarly records Perkin's appointment, yet he neither officially accepted the Chair nor taught in the College.

Young then withdrew the grant and asked the trustees to allow him to cancel the deed of foundation[4], and in July 1870 agreed to a modification of the deed to secure harmonious working with the existing Chair of Chemistry. The modified deed and the donation of £10,500 were accepted by the trustees of Anderson's University at a special meeting on 12th July 1870[5]. G. Bischof then became the first active "Young" Professor of Technical Chemistry, being succeeded by Edmund J. Mills in 1875, who specialised in lectures on the chemistry of dyes.

Penny did not merely attack Perkin: he published a pamphlet entitled "Dr. Penny's remonstrance and appeal against the nomination and appointment of an additional Professor of Chemistry in Anderson's University". One sentence in this pamphlet shows Penny's avarice, his fear of losing money, where he writes: ". . . next to honourable and honest dealing the monetary aspect of a personal question is the most important to all men". Dr. Adams, Penny's friend and physician, wrote a similar remonstrance dated 11th September 1869 and entitled "Dr. Adams' reason of protest against the appointment of an additional Professor of Chemistry in Anderson's University". Shortly afterwards Penny died of a stroke, and Adams published yet another pamphlet— a eulogy of Penny. The preface of this biography (*Biographical Sketch of the late Frederick Penny, Ph.D., F.R.S.E., Professor of Chemistry, Anderson's University, Glasgow*, by James Adams, M.D. (Glasgow 1870)) specifically states the cause of Penny's death, where we read: "During the few weeks that intervened between the beginning of the proceedings which broke up the health and led directly to the death of Professor Penny, viz. from 1st September till 22nd November 1869 . . .".

Years later Dr. Adams was still writing in defence of his old friend. In a letter dated 20th December 1893 which he wrote to Professor A. H. Sexton (then engaged on a history of the college) he says: ". . . we were close friends, rarely apart for 20 years. He died in my arms, I was his executor . . . Penny was a remarkably healthy individual, he possessed an inherited excellent physical constitution. He suddenly collapsed, mind and body— the failure . . . was a reaction of mind and body . . . Penny was incomparably the most popular lecturer . . . Dr. Penny's consulting practice was the largest in Scotland, and from reliable information given me the largest in Great Britain. I *know* that for some years before his death, his professional income exceeded £6000 a year and it was progressing. But he was not greedy on money . . ."

Penny was famous as well as wealthy. His expert evidence for the Crown helped to convict Dr. E. W. Pritchard in the celebrated aconite poisoning case. His simply outrageous solution of the North Esk pollution affair was accepted.

If this history deals at length with Dr. Penny it is because he is important to it. The world of chemical industry knows much about Perkin, but little of Penny— the man who was probably responsible for putting Perkin into the backwaters of private research and denying him the opportunity of an academic career similar to that of Hofmann or Hummell.

Penny was only 53 when he died— of wounded pride. He was the man in possession, but he was passed over when promotion came. His case is still familiar today in the academic as well as the business world, though the resulting deaths occur perhaps more lingeringly.

The full story may never be known, yet one can reason from the evidence available that Young wanted a prominent chemist other than Penny to inaugurate the "Young" Chair. He had the power, as President, to "hire and fire" and to negotiate in secret. He chose Perkin, the youthful yet famous innovator of dye manufacture, who already hankered for a return to academic life. Robert Hogg, then an active and progressive chemical merchant in Glasgow, and known to both Perkin and Young, may well have recommended Perkin. Young let the news slip and it was published in the daily press. Penny retaliated venomously and outrageously; and quickly died. Perkin recoiled from public controversy.

A Scottish dyer, Walter Crum, J.P., F.R.S., of Thornliebank's famous Calico Printing and Dyeworks, was a student of Anderson's University, and President in the years 1848–65. He was a tireless worker for the University, and his correspondence shows his power (as a President should have power) behind the scenes. He was well known to Hofmann, the early mentor of Perkin (see Fig. 7).

EARLY VOCATIONAL TRAINING IN GLASGOW

There is no available evidence of the formal teaching of dyeing, nor of any other textile subject, in Glasgow during the first half of the nineteenth century. The principles of such subjects must, however, have been taught in the Mechanics' class, because Glasgow and the area around it was predominantly a textile community. It was famous for the spinning and weaving of fine cottons, e.g. lawns, muslins, and gauzes. The population of the town had grown from 28,000 in 1765 to 90,000 in

1806. Water power was available for the mills, there were long-standing connections with the Southern States of America which ensured a supply of cotton, the port had been enlarged and the river Clyde dredged. Block printing, and therefore bleaching and dyeing, had been practised in the district in 1732, thirty-two years before it was practised in Lancashire. The area in and around Glasgow was covered with printworks. In 1828, in Glasgow alone, there were 13 of them, stretching from Anderston to Shawfield and Well Park, employing 305 journeymen printers and 243 apprentices, many of whom must have sought training in the principles of their trade [6]. Glasgow was equally famous for the dyeing arts, with such firms as the Crums of Thornliebank, the celebrated alizarin dyers and calico printers, and the Orr Ewings, pioneers of Turkey Red piece-dyeing in the Vale of Leven. There were numerous drysalters and chemical manufacturers in Glasgow, e.g. the Whites of Glasgow Green and the Tennants of Hurlet.

Whether or not there were classes in dyeing in Glasgow at that time, information on the subject was certainly disseminated through the *Practical Mechanic and Engineers' Magazine*, a journal (8d. monthly) which was printed, published and produced in Glasgow. It was first issued in 1841, its object being "to promote the education of the working classes", and it catered for all trades, reporting up-to-date ideas and information on the latest patents. During the years 1842–44 there was a series of articles under the title "Dyeing Theory and Practice". The articles read very well today and must have been very useful to dyers. The last article refers to Scheele's Green, prepared with the aid of "bluestone" and arsenious acid. The writer states that this method could be fatal to the workman, and continues: "this fact ought to stimulate dyeing improvements, e.g. moderate premiums to the workman who is too often robbed of the honour of improvements he does effect. The constant jealousy which exists amongst employees will, we fear, prevent their joining together for improvement of the general trade . . .". The final words of the article are: "Our object has been to impress upon the operative the necessity of studying the principles in conjunction with his practice— if even one of our brethren does this, our labour is not in vain."

So nearly 120 years ago in Glasgow we have evidence of one source of dyeing knowledge, which includes an explanation of the theory, descriptions of the practice, "rewards for ideas"— long before modern incentive schemes— and a forecast of the internal strife in Trade Unions.

The Mechanics' Institute of Glasgow taught those students of chemistry who could not attend day classes, the lecturers usually being the professors of chemistry at Anderson's University. In 1825, i.e. two years after its breakaway from Anderson's Institution, the Institute had 1300 enrolled students. There was great enthusiasm for education, and in 1846 the subjects taught were chemistry, natural philosophy, anatomy, history, and design. Whilst the Mechanics' Institute catered mostly for artisan workers, students with many other backgrounds attended, and one of these, William Thomson, later became famous as Lord Kelvin.

FOUNDATION OF THE WEAVING COLLEGE

The President of Anderson's University in 1866 was W. M. Neilson, an engineering industrialist with original ideas on education. He suggested about this time a scheme for a Central Technical Institute, with schools affiliated to teach skilled workmen the science of their trades. These schools or classes were to be near their homes or occupations "so as to give every facility for study in leisure hours". No one scoffed at this idea of filling in spare time after a hard day's work— the Glasgow tradesmen and apprentices wanted to learn.

It was 1871 before Neilson's ideas were adopted. At that time there was great interest in technical education— just as there is today. During the last decades of the nineteenth century Germany was pre-eminent in applied science, and her success in the Franco–German war was said to be due as much to industrial organisation based on improved technical teaching as to prowess on the battlefield. The war of 1870 therefore acted as a spur to those concerned with promoting technological education in Glasgow. In 1871, a committee whose chairman was Dr. James Young, President of Anderson's University, opened a public subscription for the new Central Technical Institute proposed by W. M. Neilson. Instead of the £50,000 aimed at, only £12,030 was subscribed, and very little of this came from the dyeing firms in the area. The main support came from shipbuilders, engineers, merchants, and some cotton manufacturers. There was only lukewarm support from the rest of the textile industry, probably because many people thought that the existing Anderson's University was sufficient.

It was eventually decided to form a Weaving College, because there was at this time no textile teaching in the city, and one-third of the money raised was allocated to this purpose. But progress was slow. There was no real enthusiasm, and only the dominant personality of David Sandeman, a textile merchant in Glasgow, aroused the cotton manufacturers to effective support. In 1877 the Weaving College was opened at Well Street, Calton, in the east of the city among the looms and spinning mills. There was no teaching of dyeing in this college, although it had been proposed at the outset. Teachers were difficult to find, because employers in the dyeing and calico printing trades would not allow their foremen or managers to teach dyeing. There was still much secrecy in the dyeworks and no desire for dyeing education amongst the big dyeing firms— had they not ignored the public subscription? Their attitude undoubtedly held up dyeing education in Glasgow: they feared that dyeing classes would disclose practical dyeing secrets. There had always been chemistry classes at Anderson's University for those in the industry who desired them, but practical dyeing instruction was not encouraged.

Block loaned by the College)

FIG. 1— John Anderson (1726–1796), founder of "Anderson's University", Glasgow, now the Royal College of Science and Technology

FIG. 2— Dr. Frederick Penny, Professor of Chemistry in Anderson's University, 1839–1870. It was probably Penny's opposition that was responsible for Perkin's refusal to accept the offer of the new Chair of Technical Chemistry. (Portrait copied from an original albumen print forming the frontispiece to the *Biographical Sketch of the late Frederick Penny*, by Dr. James Adams (printed for private circulation: Glasgow, 1870))

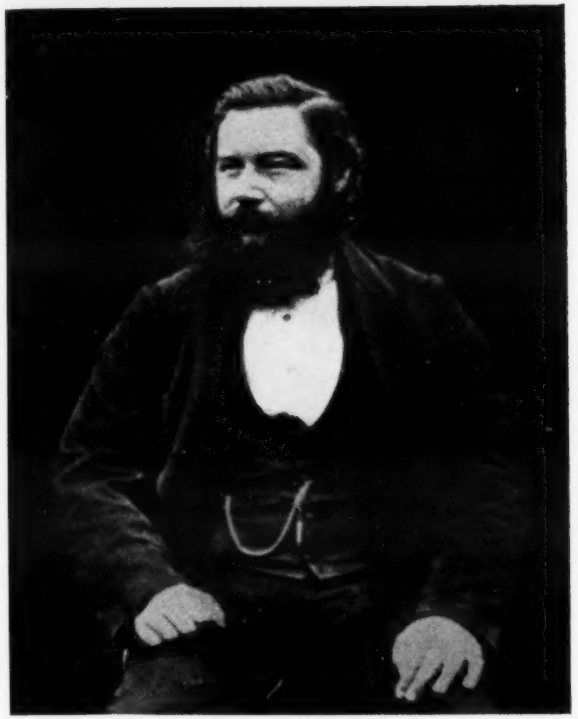
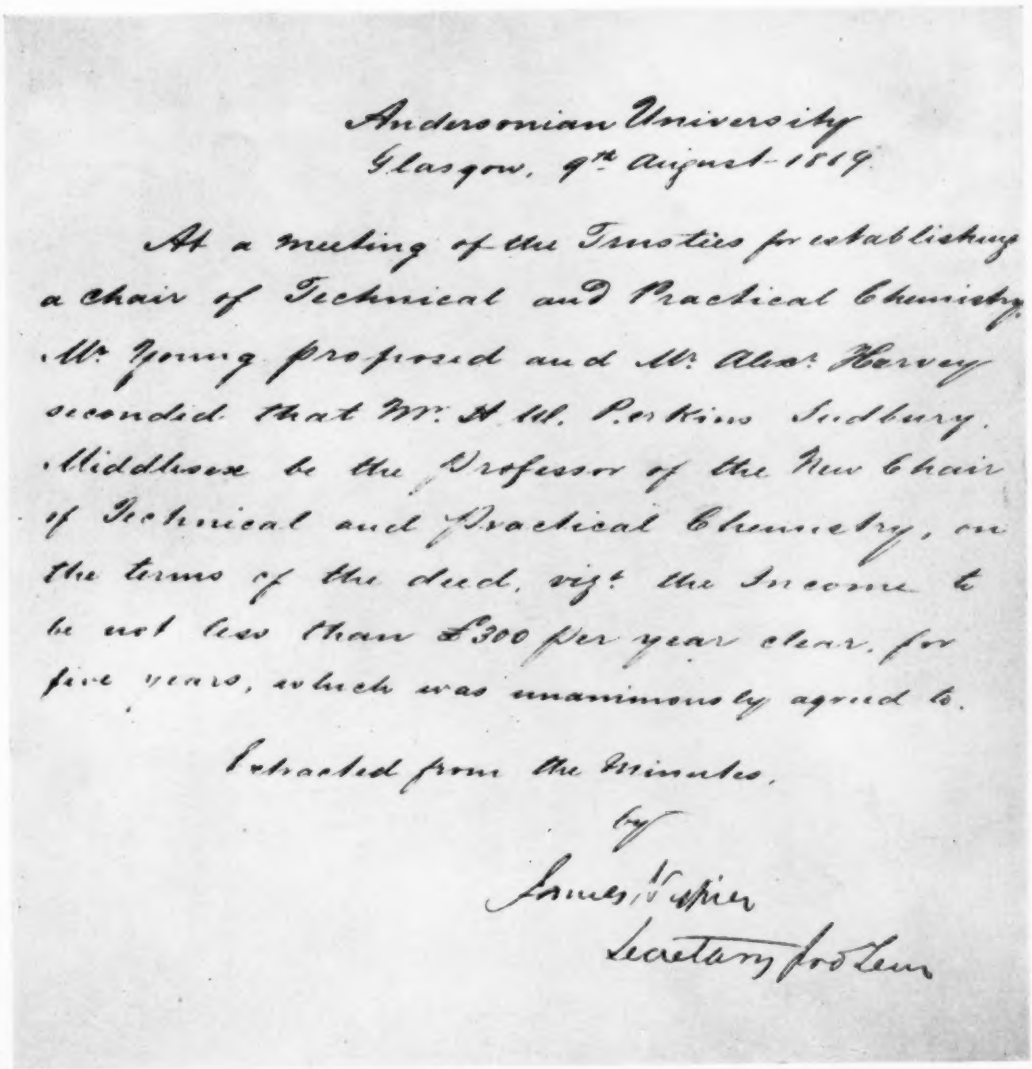


FIG. 4— W. H. Perkin at about the time of his appointment to the new Chair (Portrait copied from Fig. 1 in paper by Cliffe, J.S.D.C., **73**, 312 (1957))



Andersonian University
Glasgow, 9th August 1869.

At a meeting of the Trustees for establishing a chair of Technical and Practical Chemistry. Mr Young proposed and Mr Alex. Harvey seconded that Mr A. W. Perkins Sudbury, Middlesex be the Professor of the New Chair of Technical and Practical Chemistry, on the terms of the deed, viz. the Income to be not less than £300 per year clear, for five years, which was unanimously agreed to.

Extracted from the Minutes,

by

James Napier

Secretary pro tem

FIG. 3.— Extract from the minutes of a meeting, held on 9th August 1869, at which it was decided to appoint Perkin to the new Chair. Note the mistakes made in quoting Perkin's initials and surname

W. H. Perkin Esq. (Copy)
Sudbury
London

Andersonian University
Glasgow 8th Sept 1869

Dear Sir

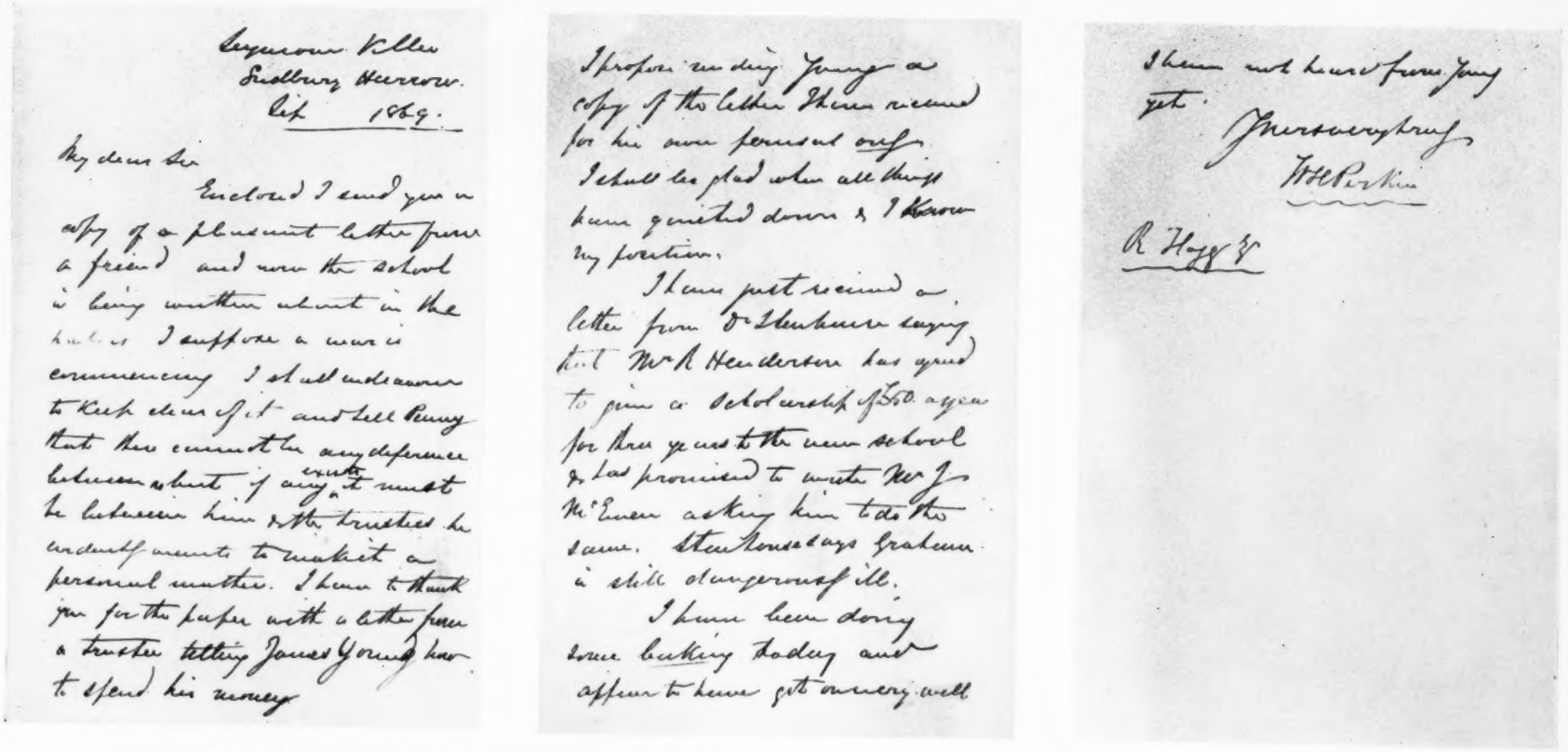
Observing from the announcements in the Glasgow Herald Newspaper that you have accepted the Chemical appointment under Mr. James Young's Trust, I feel it due both to you & myself as brother professionals on terms of friendship, to let you know thus early that I regard this appointment not only as antagonistic but as very injurious to my interests in connection with the Anderson's University and consequently that I strongly object to your intrusion upon my province as the Professor of Chemistry.

The grandeur of my objection is that you are appointed to equal status in the same institution, & will have the opportunity & will indeed be placed under the necessity of endeavouring to supersede me

in the discharge of
duties specially assigned
to me, and of taking
emoluments which have
hitherto been my prem
-ium and indeed my
principal recompense
and privilege. In kind
-ness to you I have deemed
it proper not to allow
you to be ignorant of
my feelings in regarding
this matter, but what-
ever may arise out of
it I hope nothing will
occur to affect our good

feeling.
I remain
Yours truly
(sgd) Frederick Penny

FIG. 5— The letter in which Penny advises Perkin of his (Penny's) objection to the creation of a new Chair of Chemistry (copy in Perkin's handwriting (?) found with the Robert Hogg correspondence (Andersonian Library))



Sequoia Villa
Sudbury Harrow.
Oct 1869.

My dear Sir

Enclosed I send you a copy of a pleasant letter from a friend and now the school is being mentioned about in the Indian I suppose a move is commencing I shall endeavour to keep clear of it and tell Penny that there cannot be any difference between about if any route it must be between him & the trustees he evidently wants to make it a personal matter. I have to thank you for the paper with a letter from a trustee telling James Young how to spend his money

I propose sending Young a copy of the letter I have received for his own personal ends. I shall be glad when all things have quieted down & I know my position.

I have just received a letter from Dr Thomson saying that Mr R Henderson has agreed to give a scholarship of £50 a year for three years to the new school & has promised to write Mr J McEwen asking him to do the same. Stenhouse says Graham is still dangerously ill.

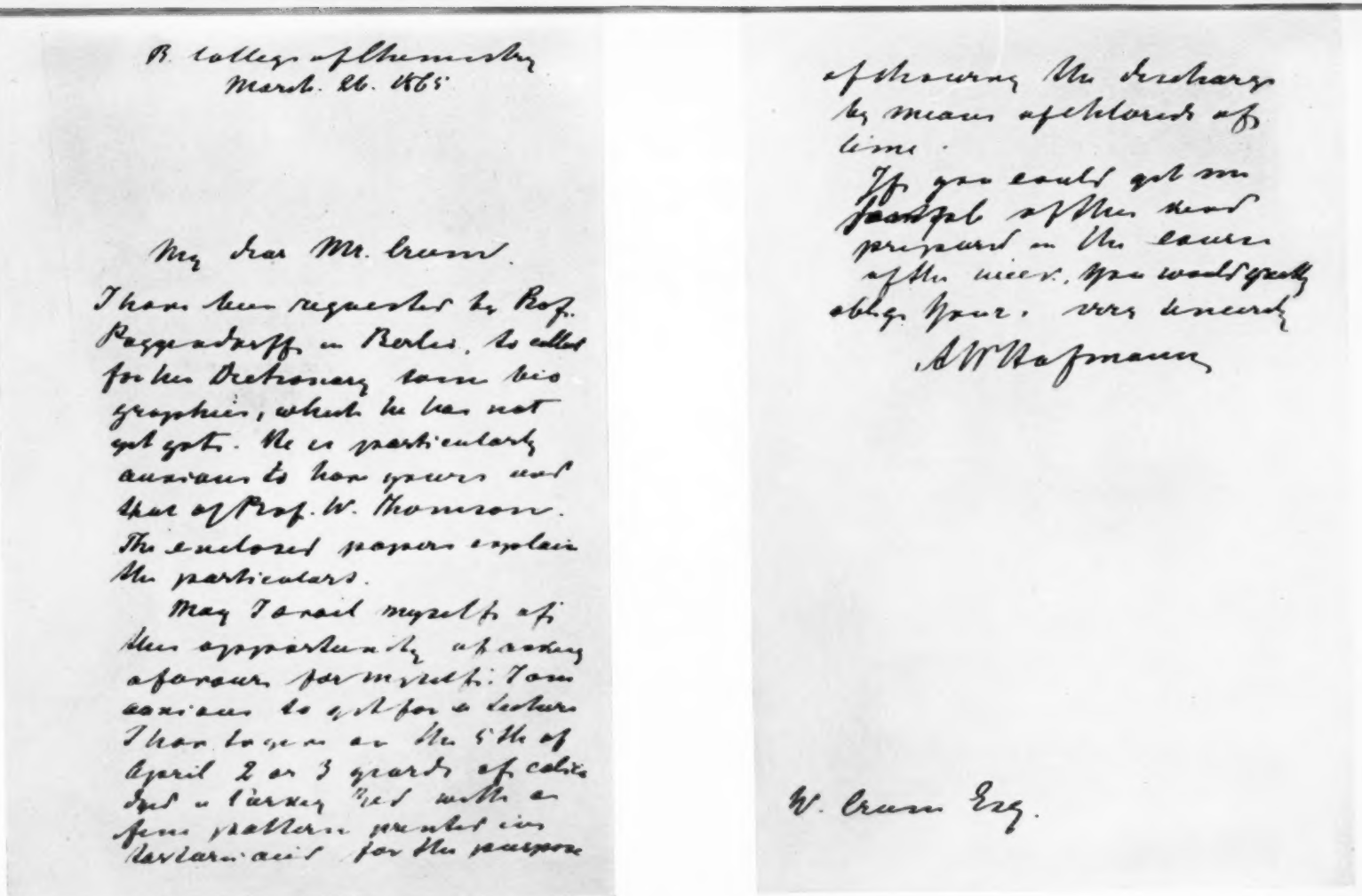
I have been doing some banking today and appear to have got on very well

I have not heard from Young yet.

Yours very truly
W H Perkin

R Hogg Esq

FIG. 6— Original of letter by Perkin to R. Hogg, of Glasgow, in which he hints at declining the offer of the Chair. Note the omission of the day of the month



R. College of Chemistry
March 26. 1865

My dear Mr. Crum.

I have been requested by Prof. Poggendorff, in Berlin, to collect for his Dictionary some biographies, which he has not yet got. He is particularly anxious to have yours and that of Prof. W. Thomson. The enclosed papers explain the particulars.

May I avail myself of this opportunity of asking a favour for myself. I am anxious to get for a lecture I have to give on the 5th of April 2 or 3 quarts of coloured but clear gas with a few platinum points in Geissler's tubes for the purpose of showing the brilliancy by means of the lamp of Bunsen.

If you could get me [illegible] prepared in the course of the week, you would greatly oblige Yours very sincerely

A W Hofmann

W. Crum Esq.

FIG. 7— Letter from A. W. Hofmann to Walter Crum, President of Anderson's University, 1848–1865. Their close acquaintance may have been an indirect cause of W. H. Perkin's being offered, in 1869, the first appointment to the Chair of Technical Chemistry in Anderson's University. Perkin had been a pupil of Hofmann at the Royal College of Chemistry, London, 1853–1856. (*Presented by A. W. Murray*)

FIG. 8— Incorporated Weaving, Dyeing, and Printing College, Calton, Glasgow, 1877–1908. View taken in 1908 just before the college was incorporated in the Glasgow and West of Scotland Technical College. (From Blair's *History of the Glasgow Weaving College*)

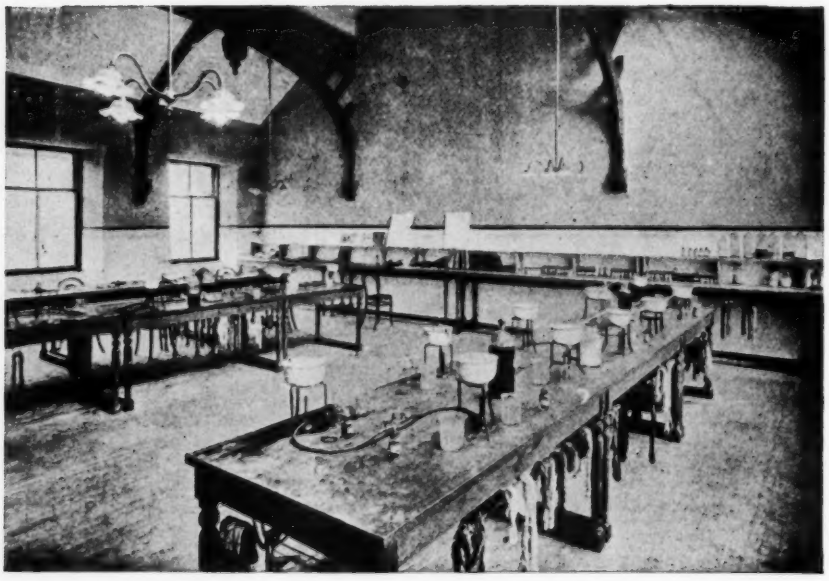


FIG. 9— The dyeing laboratory in the Weaving College, 1908. (From Blair's *History of the Glasgow Weaving College*)

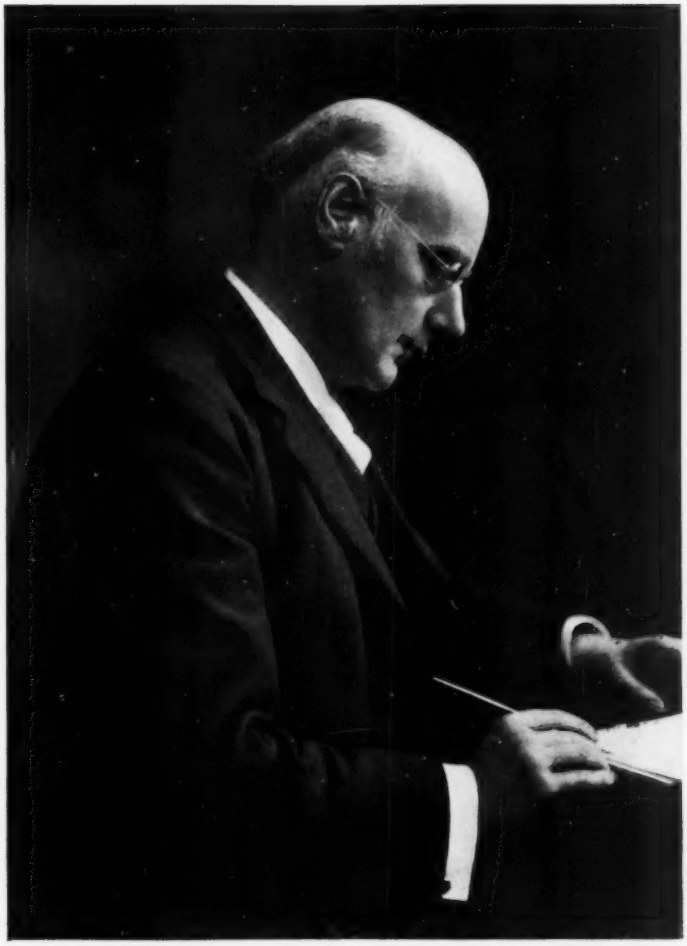
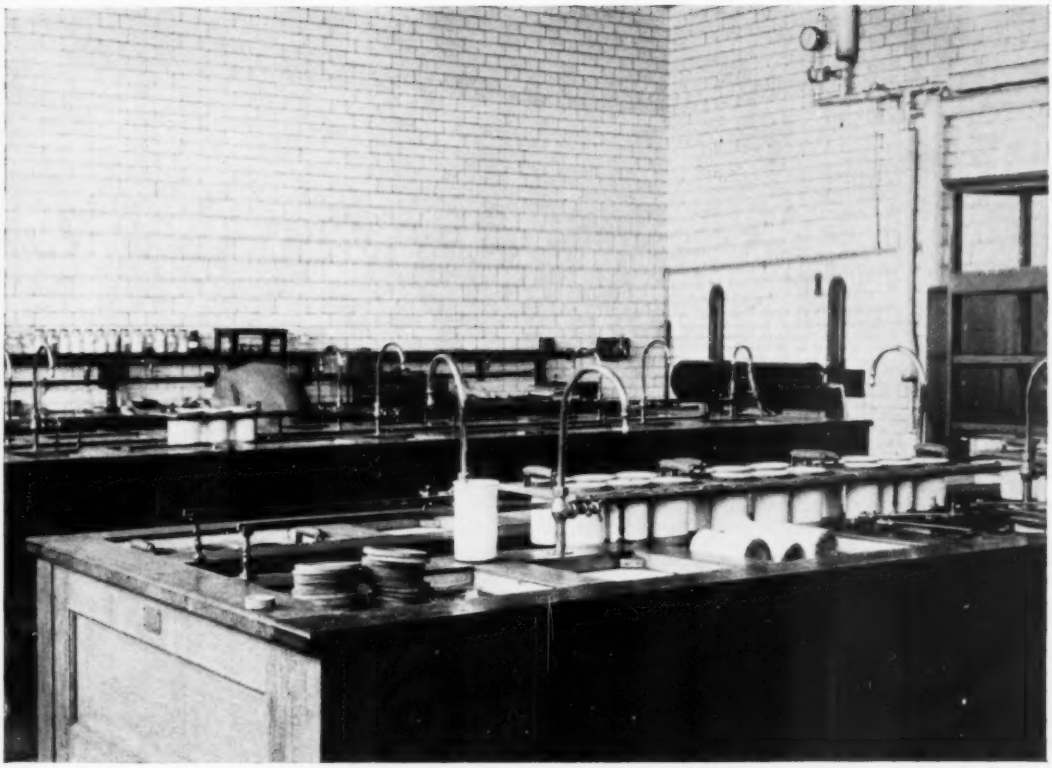


FIG. 10— H. F. Stockdale, Secretary (later Director) of the Technical College, who was largely responsible for the new building plans and for the taking over of the Weaving College

FIG. 11— Drawing (ca. 1910) of the new building for the Glasgow and West of Scotland Technical College. The façade has remained almost unchanged to this day. This view shows the south frontage, on George Street. The dyeing laboratory is on the top (fourth) floor, the windows being visible immediately below the centre gable

Photograph by A. Speirs

FIG. 12— A. B. Steven (right), first lecturer in dyeing in the Technical College, 1908–1945, with his successor, C. H. Giles. (Photograph taken in September 1959)



Photograph by C. H. Giles

FIG. 13— The main dyeing laboratory, in May 1946, before alterations. It was then probably in almost the same state as when opened in 1908. Note the benches with water-baths for heating dyepots, similar to those then installed at Leeds University. New dyeing laboratories are included in plans for a new building for the Department of Chemical Technology and the Department of Chemistry. Building is expected to start soon

DYEING, BLEACHING, AND PRINTING.

The course of instruction will consist of two series of lectures on one evening per week each during the winter session. Course I., Dyeing; Course II., Calico Printing. Each course will be complete in itself, and will be supplemented by practical instruction in the Dyeing and Printing Laboratories.

Students without previous chemical training are strongly advised to attend a course of Chemistry, as they will find it of the greatest service for a proper understanding of the work.

DYEING.

Tuesdays, 7 to 8.

The Textile Fibres.—Wool, silk, cotton, flax, jute, ramie, artificial silk, etc.—their origin, structure, chemical and physical properties, and behaviour with the various chemicals employed in bleaching, dyeing, etc. Detection of the various fibres.

Preliminary Operations.—Wool and silk scouring and bleaching; cotton and linen bleaching. The most important methods of carrying out these operations, the machinery and chemicals employed, and the principles underlying their use.

Water.—Impurities; effect in scouring, bleaching, and dyeing. Detection and removal of impurities. Treatment of waste effluents.

Mordants.—The preparation, properties, and methods of application of the more important mordanting and fixing materials. Metallic salts, tannins, oil mordants.

Machinery.—The processes and machinery employed in the dyeing of the various fibres in different stages of their manufacture—*e.g.*, loose material, yarn, slubbing, cops, and piece goods.

Colouring Matters.—The chemical characteristics and methods of application to the various fibres of the different classes of colouring matters, (*a*) mineral colours—Prussian blue, chrome yellow, iron buff, etc.; (*b*) natural colouring matters—indigo, logwood, fustic, cutch, cochineal, red woods, etc.; (*c*) artificial colouring matters—direct cotton dyes; acid, basic, and mordant dyes; sulphide dyes; indigo and other vat dyes; aniline black, para red, etc. Dyeing of union materials; stripping of shoddy; fastness of the various dyestuffs to light, washing, milling, etc.

Finishing.—The most important operations of finishing wool, cotton, and linen materials.

Fee for the Course, 7s. 6d.

CALICO BLEACHING AND PRINTING.

Thursdays, 7 to 8.

Cotton and Linen.—Their origin, structure, physical and chemical properties, and behaviour with the usual chemicals employed in practice.

Operations preliminary to Printing.—Singeing, bleaching, etc. The machinery and chemicals employed, and the principles underlying their use. Madder bleach, Turkey-red bleach, etc.

Water.—Impurities; their detection, and effect in bleaching and printing. Water purification and treatment of waste effluents.

Mordants.—Preparation, properties, and methods of application of the more important mordanting materials. Metallic salts, tannins, oil mordants.

Thickening Materials.—Their properties and application. Starches, flours, natural and artificial gums, dextrines, etc. Colour mixing, straining, etc.

Machinery.—The various types of printing machines, steamers, drying machines, etc., employed in practice.

Colouring Matters.—(*a*) Mineral colours, chrome yellow, Prussian blue, etc.; (*b*) natural dyestuffs—indigo, logwood, cutch, Persian berries, quercitron bark, etc.; (*c*) artificial dyestuffs—direct cotton dyes, acid dyes, basic dyes, mordant dyes, indigo and other vat dyes, aniline black, sulphide dyes, azo dyes developed on the fibre. Application of the above colouring matters to cotton and linen.

Printing Styles.—Dyed style, steam or extract style, madder style, indigo and aniline black styles, para red styles, reserve or resist styles, discharge styles.

Finishing.—The chief processes and machinery employed in the finishing of printed materials.

Fee for the Course, 7s. 6d.

LABORATORY.

The Laboratories will be open on *Mondays, Tuesdays, and Thursdays from 7 to 10. As a rule students who propose to work in the laboratories will be expected to attend at least one of the lecture courses.

The course of instruction is designed to acquaint the student with the principles involved in the various operations of scouring, bleaching, dyeing, and printing. (For details see p. 91.)

Each student is supplied with a set of six steam-heated dye baths for experimental dyeing, and also with a bench for analytical work.

Fees—One evening per week, 30s.; two evenings, 40s.; three evenings, 50s.

*Subject to alteration.

FIG. 14— Copy of syllabus of the first evening classes in dyeing, etc., in the Technical College. (From the College *Calendar*, session 1908–1909)

In 1883 Henry Dyer, addressing the important Glasgow Philosophical Society on "Technical Education", specially mentioned the Weaving College. He said it was "successful as far as its means permit", but connecting schools were required, e.g. for dyeing, bleaching, and calico printing. In 1899, the Yorkshireman, Sir Swire Smith. spoke in Glasgow on "Technical Education— stands Glasgow where it did?" He said that the Weaving College needed more support, and that the Germans were superior in textile colour and design because of the scientific knowledge acquired by their dyers in the technical schools.

It was not until 1899 that dyeing was taught. In that year the College title was registered as "The Incorporated Weaving, Dyeing, and Printing College of Glasgow" (see Fig. 8 and 9). W. McConnell, F.C.S., lectured on wool and cotton dyeing for two years, until succeeded by W. Jackson, F.C.S., chemist at the printing works of John Glen, Caldercruix, near Glasgow. By this time the employers' attitude had changed— there had been widespread mergers of English and Scottish dyeing and calico printing firms. There was less secrecy, and personal contacts within the industry had developed. Newcomers from the South had been taught dyeing, and they in turn encouraged its teaching in Glasgow. The classes in these early days were held on Saturday afternoons. Good progress was made in the teaching of dyeing and printing, and in 1904 the College won its first City and Guilds of London Medal (Silver Medal for dyeing, awarded to W. J. Palmer).

Engraving for calico printing was taught in 1905: this was the first class of its kind in Great Britain. The teacher was William Blackwood, engraver at the South Arthurlie Printworks, Barrhead, who later published a book on the subject (*Calico Engraving* (London: Charles Griffin & Co. Ltd., 1913)). A textile colouring class, in conjunction with the Glasgow School of Art, commenced in 1906. It was specifically for "that class of young men employed in the textile and allied trades who as manufacturers, calico printers, salesmen, buyers, etc., will in the future direct and influence textile design". No mention is made of women employees: the successors of Anderson did not have his vision.

There were yearly exhibitions of coloured textiles such as French silks, Oriental rugs, Early English fabrics, and Paisley shawls. These exhibitions were organised by a Governor of the College, Matthew Blair, who had been a drawboy in Paisley when shawl making was in its heyday. The 1900 exhibition aroused so much interest (two shawls were loaned by Queen Victoria) that he was encouraged to write on the subject. His book, *The History of the Paisley Shawl*, a classic, was the direct outcome; so too was the collection of shawls now housed in the Paisley Museum. Matthew Blair also wrote *The History of the Glasgow Weaving College* (Paisley: Alex. Gardner, 1908) and encouraged the formation of dyeing classes. He was a partner in a firm of yarn merchants which still flourishes in Glasgow.

FIG. 14— Copy of syllabus of the first evening classes in dyeing, etc., in the Technical College. (From the College *Calendar*, session 1909–1909)

AMALGAMATIONS AMONG GLASGOW'S TECHNICAL INSTITUTIONS

The Weaving College had taught 1800 students in textile subjects, including 250 for dyeing and 90 for engraving. It was a specialised college and as such kept itself a little apart, so the great amalgamation of 1886, when the technical schools of Glasgow united, left the little weaving school untouched. This amalgamation, which was instigated by the Scotch Education Department, merged Anderson's College (formerly Anderson's University), the College of Science and Arts (formerly the Glasgow Mechanics' Institution), Allan Glen's Institution (founded in 1843), and Atkinson's Institution to form the Glasgow and West of Scotland Technical College. It was, in effect, a reunion of the scattered offspring of Anderson's original Institution under one leadership and in one set of premises. The old "Andersonian" students covered a wide range of occupations. The *Calendar* for 1872–3 shows the variety and the number of students from each trade, thus: dyers, 15; engineers (mechanical), 121; druggists, 60; drysalters, 3; bank tellers, 2; brewer, 1; builder, 1; flesher, 1; bakers, 3; chandler, 1; clothlappers, 4; engravers, 11; gardeners, 3; hamcurer, 1; Inland Revenue officers, 7; warehousemen, 100; insurance agents, 2; message boys, 4; shipwrights, 4; soapmakers, 2; medical students, 12 . . . The dyers at any rate were three times as numerous as "the butcher, the baker, and the candlestick-maker"!

In 1908 the Weaving College was amalgamated with the Glasgow and West of Scotland Technical College, which had for many years wished to control it. This amalgamation came about only after years of negotiation. In 1902 a joint committee of the two colleges studied a scheme of amalgamation prepared by H. F. Stockdale, the Secretary of the Technical College (see Fig. 10). This scheme proposed that the Weaving College should become the Textile Department of the Technical College. The Governors of the former "received the draft scheme favourably" but avoided commitments, and it was four years before further official meetings again took place. In 1906 Stockdale convened another meeting of representatives of the two colleges "to consider the recent report of inspection of the Technical College by the Scotch Education Department", which stated: "The absence of classes in dyeing and bleaching from the college curriculum struck me as specially noteworthy". The Inspector had further stated that "dyeing classes were apparently provided to some extent by the Glasgow Weaving School", and he expressed the hope that the chemical laboratories of the Technical College would be used for dyeing studies.

The Weaving College Governors were in an awkward position, since they admitted that the chemistry side of their dyeing classes was not good enough. They could not ignore the comments of the Education Department, and they agreed that students of dyeing and textiles should study chemistry at the Technical College, two evenings per week: "The first hour lecture, the remainder to

be laboratory work". The fees were fixed at 30s. and the number of students at 20 per class. No decision was reached on combining the dyeing with the chemistry classes.

Further discussions between the two colleges continued. The Weaving College representatives suggested a form of union between the two which would prevent complete control by the Technical College. This proposal was rejected, and Stockdale made the following points in reply. "The Technical College possesses the finest school of chemistry in Scotland, possibly in Great Britain, it cost £50,000 and requires £4000 p.a. to maintain, the whole of this for applied science. You agree that dyeing students require thorough grounding in principles of chemistry, and we will provide it and relieve you of dyeing classes." The note continued: "although there is not the same close connection between weaving and the engineering sections of the Technical College as there is between dyeing and chemistry— yet the work should be under one authority and we recommend amalgamation".

DYEING CLASSES AT THE TECHNICAL COLLEGE

In November 1906 the trustees of T. Graham Young [7] offered £10,000 to provide for the teaching of dyeing and bleaching "under the Chair of Technical Chemistry" and "hoped that students of the Weaving College would participate in this great scheme". After this offer, the proposed union was virtually settled, and Dr. Thomas Gray, Professor of Technical Chemistry, with W. M. Stockdale, the Secretary, set off on a round of visits to the dyeing schools at Leeds University and the Municipal Technical Colleges in Bradford and Manchester. Following their visits it was agreed, in January 1907 [7], that "provision be made for giving instruction in the methods of testing the dyeing properties of colouring matters by means of experiments in beakers in a suitably equipped laboratory . . . with appliances for large scale experiments for dyeing 5 to 10 lbs. of material in one operation . . . The laboratory should be $31' \times 29'$, for 24 students, with smaller accommodation for the balance room and the pattern room, a store room and a laboratory to accommodate winches, vats, jacketted pans (10 and 20 gallons for dyeing loose wool), 1 jigger, an experimental printing machine, a steamer, a hydro extractor and one experimental finishing machine".

The joint committee of the two colleges agreed to purchase the St. Paul's Church site, adjacent to the Technical College, for erection of the building to house the new Textile Department, which would cost £12,500. The money was to be raised partly by sale of the Weaving College premises, partly by a grant from the Scotch Education Department, and partly by industrial subscription. In addition, a sum of £10,000 was earmarked for the new dyeing laboratories and teaching. In October 1907 the amalgamation was finally approved to take effect on 31st July 1908, but the plans appear to have been altered, probably at the suggestion of Professor Gray, and the Textile Department and the dyeing laboratories were actually incorporated in the west end of the top floor of the main building adjacent to the Department of Technical Chemistry, and not in a separate extension (see Fig. 11). No records to explain the change of plan have survived.

The minutes of the joint committee meetings during the years 1902–8 clearly reveal the hidden struggle for control of the Weaving College. It was the absence of scientific dyeing instruction which enabled the Technical College to absorb the whole of the Weaving School— looms and all— and Stockdale, the capable Secretary of the Technical College and of the joint committee, was the architect whose plans made the union a success.

In February 1908, fourteen applicants answered the advertisement for a teacher of dyeing at a salary of £250 per annum, and from them Alex. B. Steven was chosen and appointed Lecturer in Dyeing and Bleaching (see Fig. 12). He was a distinguished student of Sir William Ramsay at University College, London, and of the Dyeing Department of the Yorkshire College (later to become Leeds University), and had lectured at Leeds for the previous five years.

The new dyeing laboratories were opened for evening classes in September 1908 (see Fig. 13), with 21 students for dyeing and 23 for calico printing lectures (see Fig. 14). Day classes in these subjects were started in 1909, and in 1914 a three-year diploma course in dyeing commenced. These day classes were poorly attended, the numbers never exceeding five until a large influx occurred after the 1914–18 war, when the title of the classes was changed from "Dyeing and Calico Printing" to "Dyes and their Applications". Between six and twelve students attended annually until after the second world war.

The evening classes fluctuated in numbers in a similar way, although they always attracted more students than the day classes. Immediately after the last war there was again a large class, but the numbers later fell to a level which varies little from year to year.

In 1931 the college minutes noted: "as there was a lesser demand for laboratory instruction in Dyeing, it was agreed with the approval of Dr. Gray and Mr. Steven, that the greater part of the large-scale Dyeing Laboratory be surrendered to Pharmacy". This is a revealing minute. The dyeing trade, like the textile trade in general, was in the grip of the great depression. There were few students, and little use was being made of the laboratory dyehouse machines. So the dyeing laboratories lost much of their space and, inevitably, some of their prestige. Large-scale dyehouse machinery is expensive to install and maintain, and, in the opinion of the present author, it is better to use small-scale laboratory machines— there is always work for these, but seldom enough for the large-scale plant. Whilst large-scale machines may be of temporary interest to the day student who has never visited a dyehouse, they are of little use to the evening student who is familiar with them in his daily work.

In 1945 A. B. Steven retired, and was succeeded in April 1946 by Dr. C. H. Giles (see Fig. 12), from

the Dyestuffs Division of Imperial Chemical Industries Ltd. Lecture and laboratory classes are now given to undergraduate and post-graduate students in the Department of Chemical Technology, and to students of textile technology. Evening classes are also held. Some of the courses in dyeing, in dye and textile chemistry, and in colorimetry are covered by Dr. Giles's book *A Laboratory Course in Dyeing*, published by the Society. Post-graduate research students (many from abroad) in the laboratory read for the Ph.D. degree of Glasgow University, or the Post-graduate Diploma in Research Methods awarded by the college. The researches of the laboratory currently embrace various aspects of surface chemistry and adsorption, the chemistry and physics of colour, the physico-chemical mechanisms of dyeing, and the light fading of coloured materials. The results of these researches in recent years have appeared in papers in this *Journal* and elsewhere.

PROSPECT FOR THE FUTURE

This survey was begun in 1958, the 50th anniversary of the founding of the new dyeing laboratories in the Glasgow Technical College. It was also the 50th anniversary of the Scottish Section of the Society of Dyers and Colourists, which originated in the year of the union between the Weaving College and the Technical College. For many years the Society met in the Technical College for lectures, and certainly for more than 50 years the Scottish Section has furthered the cause of dyeing education in Glasgow. But, in the opinion of the present author, the teaching of dyeing in Glasgow has never received the support from local industry that has been given to the schools at Leeds University, the Bradford Technical College (now the Bradford Institute of Technology), and the Manchester College of Technology (now the College of Science and Technology). The big dyeing and printing firms which had not supported the Weaving College of the 1870's became merged with English companies in joint-stock promotions towards the end of the nineteenth century, and it was the Scottish works which were closed down when the years of depression came. There had never been enough well-educated native managers. The talent was there, and is still there— many of the leaders of the largest dyeing and dye-manufacturing firms in England today are Glasgow Scots.

The same difficulty faces all technological education in Scotland. In an editorial headed "Decline of Scotland", in the *Glasgow Herald* of 20th July 1959, the writer complains that "Scottish firms, with few exceptions, do not show the same enthusiasm as their English competitors either in the promotion of fundamental research or in the higher technical education of their employees . . .". However, there are now signs of a more enlightened attitude. Since the last war the establishment of the Department of Industrial Administration in the college has aroused wide interest in the practice of scientific management in industry, and this must in time affect the attitude of the textile industries towards scientific training and research.

Fifty years ago there were dyeing and printing works all over the Glasgow area: today most of them have disappeared. Yet the survivors are virile and produce high-class work, especially with the new man-made fibres. The area is ideal for the manufacture and dyeing of synthetic fibres. There is pure water, a clean atmosphere, hydro-electric power, port facilities, and textile workers with inherited skill.

The training facilities provided by the dyeing laboratories at the college should be more often used by firms in the West of Scotland. Thus supported, the college could give technological information and advice on the newest trends in the industry, on a wider scale than at present, and inspire a Scottish renaissance in the arts of dyeing and associated processes.

* * *

The author thanks Sir David Anderson, F.R.S.E., late Director, and Mr. G. H. Thomson, Secretary-Treasurer, of the Royal College of Science and Technology, for their co-operation in allowing him access to the college archives, Mr. C. G. Wood, Librarian of the Andersonian Library in the college, for advice and assistance in historical research, Mr. W. H. Cliffe and Dr. C. H. Giles for supplying some illustrations and information, Mrs. J. Briton and Mr. A. Speirs for their photographic work, Miss A. B. Milroy for preparing the successive versions of the MS., and Dr. W. M. Cumming and Professor P. D. Ritchie for their encouragement.

"ARDVAAR"
HELENSBURGH
DUNBARTONSHIRE

(*Received 24th February 1960*)

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[1] See Muir, *John Anderson: Pioneer of Technical Education and the College he Founded* (John Smith & Son (Glasgow) Ltd., 1950). Also Cranston, "Schools of Chemistry in Great Britain and Ireland— X. The Royal Technical College, Glasgow", *J. Roy. Inst. Chem.*, **78**, 116 (1954); and Ritchie, *Chem. and Ind.*, 762 (1959).
[2] Quoted by Muir, *op. cit.*[1].
[3] *The Glasgow Herald* (2nd Sept. 1869).
[4] *Ibid.* (22nd Sept. 1869).
[5] Brightman, *Nature*, **182**, 613 (1958).
[6] Turnbull, *A History of the Calico Printing Industry of Great Britain* (Altrincham: John Sherratt & Son, 1951). See also Peel, "Turkey Red Dyeing in Scotland. Its Heyday and Decline", J.S.D.C., **68**, 496 (1952).
[7] See the Minutes of Governors and Committees of the Glasgow and West of Scotland Technical College, 12th and 14th Jan. 1907.

ERRATUM

On p. 393 of the July 1960 issue under **Representatives on External Bodies**, at the bottom of the right-hand column under County Advisory Committee for Textiles, R. Heaton should read **R. Heaton A.R.I.C.**

THE ROYAL SOCIETY TERCENTENARY CELEBRATIONS

Opening Ceremony— 19 July 1960

In the Royal Albert Hall, London, the Queen, accompanied by the Duke of Edinburgh, inaugurated the Tercentenary Celebrations of The Royal Society, of which she is Patron. The Fellows of the Society, of which the Duke of Edinburgh is one, and many distinguished foreign scientists from 48 countries, including China and the Soviet Union, attended the ceremony held to mark the occasion. To enable The Royal Society to ring in the fourth century of its existence, the Queen presented the Society with a silver bell which was received by the President, Sir Cyril Hinshelwood.

The Queen, speaking to an audience of 4,500, referred to the occasion as the celebration of the tercentenary of the oldest scientific society in the world, which had fulfilled the hopes of its founders and King Charles II, who granted the Society's Charter. She expressed her delight at the increasing part taken by women in scientific work in this country.

The King and Queen of Sweden were present, and the King was formally admitted a Fellow of The Royal Society.

Sir Arthur Bliss, Master of the Queen's Musick, conducted the band and trumpeters of the Royal School of Music in a salute to The Royal Society which he had composed for the occasion. Many messages of congratulation had already been presented to The Royal Society; among them was one from the Society of Dyers and Colourists, presented by the President, Mr. F. M. Stevenson. In the Royal Albert Hall, messages were read by Professor D. Graffi, representing the University of Bologna, Italy; Professor J. Lecomte, representing the Academy of Sciences in France; and Sir John Eccles, President of the Australian Academy of Science.

In his Tercentenary Address, Sir Cyril Hinshelwood urged men of science to go ahead undeterred by any uncertainties.

The scene of this great occasion was very colourful, with the background the banners of the trumpeters and below them the uniforms of the band, intermingled with the glistening of their instruments. The colour was intensified as the 500 scarlet-robed Fellows— over 300 from overseas in startlingly unfamiliar robes— entered the Hall, followed by the Queen and the Duke of Edinburgh.

Official Functions

The afternoon of Monday, July 18th was devoted by the President and Vice-president of The Royal Society to the receipt in Burlington House, the headquarters of The Royal Society, of all those official visitors from home and overseas who had expressed their desire to present congratulatory addresses on behalf of the organisations they represented. It had been agreed by Council during Mr. John Boulton's presidency that our Society should make such a presentation, and a suitably engrossed document had been prepared (the black and white representation which appears on the opposite page conveys an entirely inadequate impression of the beautiful harmony of colours employed in the scroll work).

The President, Mr. F. M. Stevenson, presented this address of congratulation on behalf of the Society and conveyed, in personal conversation, to the then present Vice-president, the good wishes of Council and all the members of our Society.

On Tuesday, July 19th, the Society was represented by the President, a Vice-president, Mr. R. C. Oakley, and the General Secretary, though there was no official reception. The occasion itself was one of intense interest, extreme magnificence, and inspiring music and speeches.

On the following Saturday evening, July 23rd, The Royal Society held a Conversazione in Burlington House, which was attended by the President and Mrs. Stevenson and the Vice-president and Mrs. Oakley. This was a very informal occasion and allowed for movement of visitors to make personal contacts in a manner which had been precluded by Tuesday's event.

It was particularly colourful since all guests were in full evening dress with regalia, and the ladies in particular were a living acknowledgment of the splendour of the dyer and finisher's art and technology.

The President's Badge was a subject of not infrequent comment and questioning as he moved about among the guests, and several people took great interest in the meaning of the various emblems of which it is composed. The President felt that, despite the eminence of the many visitors, our Society had been recognised as playing a proper part.

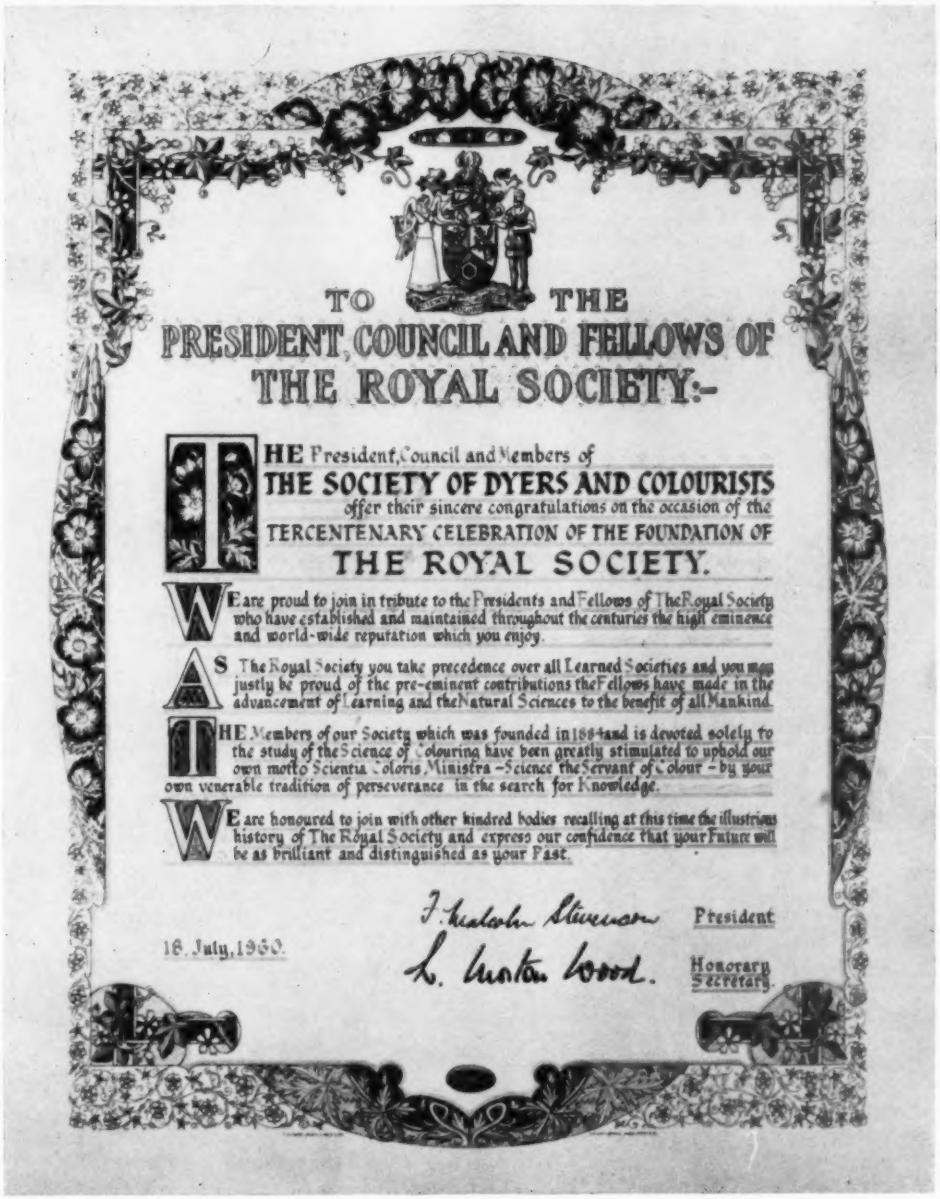
Exhibition

The Tercentenary Exhibition of The Royal Society was held in the Royal Academy of Arts, Burlington House, London, from 25th to 29th July 1960. The exhibition was arranged in fifteen sections which illustrated the wide variety of interests and achievements of Fellows of the Royal Society.

The entrance hall housed the exhibition of "Calculating Machines" illustrating the history of automatic digital computers from the first practical proposal made in 1823 up to the present day; speeds up to the order of 20 million operations per second are now obtainable. Research on computer design is beginning to suggest possible physical principles which may be operating in nerve systems and self-adaptive controllers are being developed which should improve the control of complicated industrial processes by trial and error methods.

One room of the Diploma Galleries was devoted to "Physics of the Earth, Ocean, and Atmosphere", "Exploration by Radio", "Fundamental Particles", "Solvent Extraction of Plutonium", and "Refined Chemical Separation".

During the war, the Americans separated plutonium from irradiated uranium by a precipitation process which left the uranium and the



TO THE
PRESIDENT, COUNCIL AND FELLOWS OF
THE ROYAL SOCIETY:-

THE President, Council and Members of
THE SOCIETY OF DYERS AND COLOURISTS
offer their sincere congratulations on the occasion of the
TERCENTENARY CELEBRATION OF THE FOUNDATION OF
THE ROYAL SOCIETY.

WE are proud to join in tribute to the Presidents and Fellows of The Royal Society who have established and maintained throughout the centuries the high eminence and world-wide reputation which you enjoy.

AS The Royal Society you take precedence over all Learned Societies and you may justly be proud of the pre-eminent contributions the Fellows have made in the advancement of Learning and the Natural Sciences to the benefit of all Mankind.

THE Members of our Society which was founded in 1884 and is devoted solely to the study of the Science of Colouring have been greatly stimulated to uphold our own motto Scientia Coloris Ministra - Science the Servant of Colour - by your own venerable tradition of perseverance in the search for Knowledge.

WE are honoured to join with other kindred bodies recalling at this time the illustrious history of The Royal Society and express our confidence that your Future will be as brilliant and distinguished as your Past.

J. Malcolm Stevenson President

18. July, 1960.

L. Morton Wood. Honorary Secretary.

The surrounding border is composed of three wild flowers— the blue meadow cranesbill, *Geranium pratense*; the red climbing bryony, *Bryonia diocia*; and the yellow cinquefoil, *Potentilla reptans* found on meadow banks. These three flowers represent the three primary colours which form the ground to the Society's Coat of Arms to symbolise their importance to all concerned with the manufacture and application of colour.

The Coat of Arms of the Society is heraldically emblazoned in full colours and gold and each paragraph commences with a gold initial.

fission products together. The British post-war programme required, in addition, the separation of uranium with an overall reduction in fission product radioactivity by a factor of 10^8. This was achieved by continuous counter-current solvent extraction. The exhibition illustrated the various stages of development of laboratory and pilot plant and indicated some of the fields in which basic research was necessary. The subject of "Refined Chemical Separation" was illustrated by means of exhibits on chromatography and ion exchange. Chromatography was demonstrated as a technique capable of providing the most refined separations which could be made fully automatic. Complex natural products such as pigments, sugars, amino acids, fats, etc., can be chromatographically analysed in detail and such analyses can be used for the control of industrial and chemical plants as well as for biochemical and clinical investigation.

Other sections dealt with Metals; the Molecular Structure of Biological Systems; Abnormal Haemoglobins and Human Chromosomes; Natural Selection; Microbial Genetics; Antibiotics; Vitamins; Electrophysiology; and Physiological and Biochemical Aspects of Plant Growth.

The excellently organised exhibition, which was prepared for the specialist rather than the layman, showed science at its highest level. A similar exhibition explained in simple language would be of immense interest to the man-in-the-street who will, in the long run, benefit from the discoveries now being made.

Notes

Election of a Fellow

At the meeting of Council held on 1st June 1960 the following election was made—

John Rayment

Chilwell, Nottingham; Dyeing Technologist, Chemstrand Ltd.

Society of Leather Trades' Chemists

The 1960 Annual Conference will be held in the Large Chemistry Lecture Theatre, The University, Leeds, on September 23rd and 24th. Professor W. T. Astbury, F.R.S., will deliver the Ninth Proctor Memorial Lecture on the Friday afternoon and will be Guest of Honour at the Dinner on Friday evening at the Great Northern Hotel. A detailed programme is available from Mr. G. H. W. Humphreys, Honorary Secretary of the Society, Forestal Central Laboratories, Harpenden, Herts.

Congress of "l'Association des Chimistes de l'Industrie Textile"

The 1960 Congress will be held in Mulhouse, France on September 23rd, 24th, and 25th. It will mark the occasion of the fiftieth anniversary of the foundation of the Association.

The Congress will be preceded on September 22nd by a meeting of the Council of Delegates of the International Federation of Associations of Textile Chemists and Colourists.

During the Congress, the following lectures will be given—

Friday, 23rd September

Morning—

"Scientific research in industry" by Professor Sadron (Strasbourg)–"Chemical fibres in the French, European and world economies" by M. de Precigout (Paris)–"Innovations in artificial and synthetic fibres" by M. Herrbach (Paris).

Saturday, 24th September

Morning—

"The happy marriage of natural and synthetic fibres" by M. Rieckert (Lyons)–"Practical aspects of the dyeing, printing and finishing of woven and knitted fabrics of chlorine-containing fibres" by M. Gord (Tronville-en-Barrois)

Afternoon—

"Reactive finishes arising from textile competition" by M. Marcou (Paris)— "Contribution to the study of reactive dyes in printing" by Dr. Metzger (Bâle)

A detailed programme and registration forms may be obtained from the Association, Maison de la Chimie, 28 Rue Saint-Dominique, Paris 7, France.

First International Textile Dyestuffs, Finishes, and Auxiliaries Exhibition

This exhibition, originally planned to take place in Manchester on September 22–23rd 1960, has been postponed and will now be held in the New Exhibition Hall, Harrogate on September 4–9th 1961.

Rheology of Polymers

The British Society of Rheology will hold a meeting on the rheology of polymers at Swansea on 8th to 10th September 1960. Full details can be obtained from Dr. M. F. Culpin, 8 The Broadway, Pontypool, Monmouthshire.

National Joint Committee on Materials Handling

Films on Materials Handling

The above co-ordinating committee of professional and other non-trading research and

development associations has available a list of about 100 films on materials handling. The list gives the size, running time, a brief synopsis and the source from which each film may be obtained. Copies of the list, price 2s. 0d. post free, can be obtained from the Secretary, National Joint Committee on Materials Handling, 32 Watling Street, London, E.C.4.

Royal Society of Health 1960 Prize Essay Competitions

Details of the above are now available from the Secretary, 90 Buckingham Palace Road, London, S.W.1.

Death of Members

We regret to report the death of Mr. Leonard Max Hesse, Mr. John W. Hirst, and Mr. Arthur Robinson.

Meetings of Council and Committees July

Council— 6th
Finance and General Purposes— 6th
Mercer Lecture— 6th
Colour Index Editorial Board— 8th
Publications— 19th
Diplomas— 20th
Fastness Tests Co-ordinating— 20th
International Relations— 27th

OBITUARY NOTICES

James Ramsay Hannay

James Ramsay Hannay was born at Govan, Glasgow, on 9th August 1873. Between the ages of 6 and 15 he was educated at the Melville Street Public School at Pollokshields and then became for 4 years a pupil apprentice to the Public Analyst to the City of Glasgow, Dr. John Clark, F.I.C. Encouraged by him he attended evening classes at the Glasgow and West of Scotland Technical College, and spread his net widely by studying mathematics, machine construction and the technology of steam and other prime movers as well as inorganic and organic chemistry and metallurgy. He continued his studies for another 6 years after he had left Dr. Clark, when he was consecutively an Assistant Chemist in the laboratory of the Cassel Gold Company (1892–93) and Principal Chemist to R. Dalglish Falconer & Co. Ltd., Calico Printers of Lennox Mill, Lennoxtown, Stirlingshire (1893–1906). In 1906 he became Chief Assistant to W. E. Kay, Chief Chemist of the Calico Printers' Association, Manchester. Five years later, he joined the firm of Glas, Glen & Co., Calico Printers of Caldercruix, Lanark, as Chief Chemist and Assistant Manager. A year later, he was appointed Works Manager to the Know Mill Printing Co. Ltd. at Entwistle, near Bolton, Lancashire, and remained there for 14 years. Subsequently he became for 8 years (1926–1934) Works Manager to J. F. & E. Caulfield, Newton-le-Willows, Lancashire; for 3 years (1934–37) a part-time lecturer at the Manchester College of Technology; and for 4 years (1937–41) Assistant to the General Manager of Liberty & Co. Ltd., Textile Printers of Merton Abbey Works, London. The remaining 19 years of his life (1941–1960) were deservedly spent in a happy and active retirement marred only by the death of his wife in 1942. He died on 5th March 1960.

This brief statement of Hannay's career affords some clues to the man himself. An earnest student with an active and receptive mind, he came into calico printing with a much wider experience than most of his contemporaries. As he matured, he added to these gifts a second, critical faculty and a power of concise and clear self-expression. Consequently, his views were always respected even when they were not willingly accepted. He was perhaps born a generation too soon, when calico printing was still a jealously guarded craft in which a young and forward-looking chemist was often regarded with dismay and could advance only by taking on the cares and responsibilities of works management. He might have been happier if fate had allowed him to devote his energy and ability wholly to research and development. Nevertheless he was never unhappy. Throughout a long and active career he philosophically took life as it came and made the best of it. Near the end of his long life he could write: "Life has been good to me and I would not wish my passing to cast a shadow over those who are left".

I first met Hannay a few months before the late Dr. A. W. Crossley, the first director of the British Cotton Industry Research Association, persuaded him to join a committee representing member firms which was being formed to expand and help to control a meagre programme on bleaching, dyeing, printing, and finishing compiled by an earlier one. Hannay threw himself into its work with characteristic enthusiasm and continued as an active and valued member for 14 years. We who are left remember with gratitude, occasionally with amusement, the frank and free exchange of ideas which characterised their deliberations in its earlier years.

Hannay joined the Glasgow Section of the Society of Dyers and Colourists in 1899 and took an active interest in its affairs for more than 50 years. He served on various committees, being for many years an active member of the Publications Committee, and became Chairman of the Manchester Section. He was also a member of the Revision Committee of the first edition of the *Colour Index* published in 1924. Awarded the Research Medal of the Worshipful Company of Dyers in 1915–16 for a paper on *The Interaction between Metallic Copper and Certain Dyes of the Thiazine, Oxazine, and Azine Series* (J.S.D.C., **31** (1915) 244–252), he had the great satisfaction of seeing his elder son, Ramsay J. Hannay, gain the same medal in 1953–54, the only occasion in its history when father and son have been so honoured.

Hannay was elected a Fellow of the Royal Institute of Chemistry in 1919. He was also a

member of the Society of Chemical Industry and the Manchester Literary and Philosophical Society, and a founder member of the British Association of Chemists.

In 1900, Hannay married Miss Elizabeth Ann Johnstone of New Abbey, Dumfries. They were a happily contrasted pair, she quiet and reserved with all the hospitality of the Scottish borders, he volatile, sometimes even a trifle irascible. They were both musical and had three interests in common at a time when families were still able to provide their own entertainment, namely, good talk, good music, and good gardening. Consequently, it was always a great pleasure to partake of their hospitality. Mrs. Hannay died in 1942 in her 73rd year, leaving one daughter and two sons, the elder of whom, Ramsay J. Hannay, has followed a career resembling in many respects that of his father.

One of Hannay's former colleagues once described him as "an earnest seeker after truth"; he might truthfully have added an earnest fighter for truth also.

R. G. Fargher

Mark Fletcher

Mark Fletcher, who died on 10th February 1960 at the age of 80, was one of the great leaders of the British textile trade and an elder statesman of the textile finishing industry. He was a member of our Society for fifty years.

The well-known firm with which he was associated was founded near Bolton by his grandfather in 1854, and expanded from cotton yarn dyeing into piece dyeing in 1893. Fletcher entered the industry in 1895, having been educated at Manchester Grammar School, to be in charge of piece dyeing and finishing. His father, Titus Fletcher, commenced the printing of linings at Whitefield in 1897 with only one machine, and about 1908 commenced the printing of vat colour shirtings at that time known as "French prints". This field of activity developed into the major speciality of the firm.

Titus Fletcher died in 1911 and the interests of the firm were thereafter largely consolidated and expanded at Whitefield, in a more specialised form, with the disposal of their yarn dyeing section.

His early experience in the trade convinced Fletcher that there was a wide field for co-operation possible amongst the firms in the textile finishing industry, even though there was great diversity in their size. This movement took place following the more purely financial amalgamations at the turn of the century. The first really successful effort in this direction was the formation of the Lining Printers' Association in 1907 of which his firm became members at its inception. They also became founder members of the Calico Printers' Federation and Fletcher was a leading figure in its work, becoming its Chairman in 1924 and remaining as such until 1952, when he was singularly honoured by being made its first Honorary Life President. He was also an Executive Member of the Employers Federation of Dyers and Finishers from its formation and was made its first Honorary Life President in 1952.

He led the Calico Printers' Federation through the difficulties of the 1930's, and took part in all the joint discussions which led up to the Enabling Bill and the Cotton Industry Act of 1939.

Despite the fact that so much of this work was nullified by the war, he continued to give leadership during the period of concentration and also through perhaps the more difficult post-war years including 1949, when the Federation carried out its own redundancy scheme.

He could never have carried out all these difficult tasks had it not been for his great personal integrity, courage, and profound gifts of diplomacy and patience which inevitably gave him the trust and admiration of all in contact with him. He always kept the happy knack of being at one with his surroundings, and this could well be a works bowling competition or a cricket match against the local village team.

He had no children and his wife pre-deceased him. His funeral took place at St. Asaph, North Wales, and a Memorial Service was later held at Stand Parish Church, Whitefield, and was attended by a great number of his friends and colleagues.

J. W. Reidy

Harry Birchall

Harry Birchall died on 21st March 1960 after a brief illness. He was born in Bolton, 3rd January 1910; educated at the County Grammar School there and received his technical training at Manchester College of Technology, where he was awarded the Associateship.

Birchall joined the British Cotton and Wool Dyers' Association Ltd. in October 1925, and worked in the Head Office laboratory under the late Christopher Rawson until October 1933, when he was transferred to the William McConnell branch in Glasgow as works chemist. He stayed with McConnells until June 1937; then took up a similar post with Wm. North & Co. Ltd., Bradford. In December 1939 he was appointed Assistant Manager at this branch, and Joint Manager with the late Willie McCallum in December 1945, a position he held until the date of his untimely death at the age of 50.

He was elected to the General Board of Directors of The British Cotton and Wool Dyers' Association Ltd. in June 1958.

He had a wide knowledge of dyeing all textile fibres, and was an authority on the processing of cotton warps for the gaberdine trade, on which subject he gave a paper at the Harrogate Symposium of the Society in 1951, and lectured to textile societies at various times.

Harry Birchall was a man of outstanding qualities— fine character; friendly disposition; possessing a refreshing, spontaneous wit; and, withal, sound technical and administrative ability.

E. Isles

New Books and Publications

Lehrbuch der Organischen Chemie

By Paul Karrer. Pp. xx + 969 + 18 appendix + 70 index. Stuttgart: Georg Thieme Verlag. 13th edition 1959. Price, DM 60.00.

The first edition in German of this well-established textbook appeared in 1927, and the first English edition in 1938. The book, in either language, has been a favourite with students, teachers, and working chemists throughout its existence. It has been particularly valuable to those engaged in the dyestuffs and dyeing industries for its sound treatment of aromatic chemistry, and of colour chemistry. Although the present edition is claimed to be a new work, and re-written with the collaboration of distinguished specialists, it does not quite satisfy the requirements of the present day. The sections on dyes appear substantially the same as in the previous 4th English edition, with some expansion of the chemistry of the phthalocyanines and polymethins.

A new chapter covers synthetic macromolecular substances and rubber, but is restricted in all to 23 pages. This treatment is not sufficiently deep to warrant its recommendation to those engaged in preparation for the paper on polymer chemistry forming part of the A.S.D.C. examination.

The natural products, and in particular protein chemistry as applied to biochemical problems, have been brought quite up-to-date; and in other parts, for example, there is an introduction to conformational analysis and also to tropolones.

Modern views on mechanism of reactions have been introduced from chapter to chapter, but are mainly "written-in" to the older text. The main bulk of valuable factual organic chemistry remains as sound as ever, with additions of more recent or topical subjects.

On the whole it is felt that the present work is an uneasy compromise between the factual "reagents and end-products" organic chemistry of the 1920–1930 decade (covered so adequately and excellently by the earlier editions), and the "mechanism of organic reactions-cum-stereochemical/structural" treatment of organic chemistry so favoured in this country since 1950. For students now following honours degree courses in chemistry and applied chemistry in this country the present German edition is no great improvement on the last English edition as regards basic factual organic chemistry, and is considered inadequate now in its treatment of the subject from the modern theoretical stand-points. The book is beautifully printed on a high quality thin paper to reduce bulk, and well bound as in earlier editions.

R. L. Elliott

Knitterechtmachen in Rezeptform Hochveredlung von Textilien

By R. Günther. Pp. 242 including advertisements. München-Gladbach: Lapp-Verlag. 1959. Price, DM 9.85.

The author has successfully applied in this volume the technique he employed with his treatment of waterproofing (J.S.D.C., **74** (1958) 308). He has divided the field into four sections, the first of which is an association of methods depending on mechanical and physical treatments such as the setting of man-made fibres or impregnation with salts. With the second section comes crease-resistant finishing, as it is commonly interpreted. Phenol–urea and melamine–formaldehyde; the catalysts, softening agents, and many other factors are discussed. Permanent embossing is also included in the section, which embodies working recipes based on a large number of proprietary resins.

The third section deals with minimum-iron finishing and again gives recipes based on trade resins. A fourth section concerned with test methods completes the volume.

In dealing with what are probably the highest achievements of textile chemistry so far— resin-finished prints— the author has quite rightly named names. Clearly the variables would be overfacing if the finisher could not depend on standardised speciality chemicals and he has been fortunate in having Günther to catalogue these products in recipe form.

The book is fairly robust and fits the pocket in size and price. Anyone concerned with resin finishing should have his personal copy.

S. R. Cockett

Printing Ink Technology

By E. A. Apps. Pp. xxii + 552 + xi plates + iii tables. London: Leonard Hill (Books) Ltd. 1958. Price, 70s. 0d.

Students and technologists have for a long time hoped that an up-to-date and comprehensive British textbook would appear dealing with printing ink technology more appropriately than American publications in this field. This book goes a very long way towards fulfilling the need and such improvements as are required will no doubt be taken care of in a revised edition. The comments which follow are put forward essentially with this in mind.

By collecting such an imposing amount of data, the author has set himself a difficult problem in presentation. Some sacrifice in readability has had to be made to ensure a full catalogue of products in the relevant sections, e.g. synthetic resins for various types of ink. This, however, has the compensating advantage that references to individual products can be made through the highly detailed index. The latter undoubtedly merits the use of sub-headings and bold type where numerous references are given under one major heading.

In addition to the major sections on raw materials, testing and principal processes, several specialised chapters provide detail on the theoretical and practical aspects of colour, rheology, and ink–paper relationships. All these are well presented and give useful additional references for further reading. Throughout the book tables, diagrams and illustrations are intelligently employed to supplement the text, although the

number of plates is rather smaller than one would like to see in a book of such scope. In the sections on raw materials, more selective emphasis could have been placed for the benefit of students on those products of principal importance to the formulator.

The use of the term "oil adsorption" for such an old-established, empirical and none-too-reliable test for pigments is rather surprising. Apart from the controversial distinctions involved, the definition on page 117 would appear to rule out use of the revised term for the Gardner method included on page 245. In most sections limited treatment is given to the properties and uses of coloured pigments and one would like to see more detail given on suitable pigments to use in inks for three- and four-colour work, specialised packaging, and tin printing. For reference purposes, the chapter on organic colours will certainly be found of value despite some minor inaccuracies, e.g. the constitution of Permanent Red R (p. 158) which should show *o*-chloro-*p*-nitroaniline as the first component. In the gravure ink section some information on light fast dyes soluble in organic solvents would make a desirable future addition. Comments on the use of the Blue Wool Scale for measuring light fastness appear unduly pessimistic even for the time at which they were written. There is no great difficulty in using a set of blue standards for assessing fading of red prints, although experience is undoubtedly required, and the figures given in Table 17 (p. 314) are clearly of more value than the Madder scale ratings on pp. 191–2. Other testing methods and laboratory equipment are described, in many cases in valuable detail, and the only significant omission is that of the automatic muller, now widely employed in testing laboratories.

The chapters on more specialised inks, e.g. gloss, quickset, silkscreen, include worthwhile information not previously available in a textbook, and the principles involved in printing with these inks are clearly described. Similarly, the results of more recent studies on ink–paper relationships have been brought together to provide a sound basis for further reading. Factors governing the operation of all the more important types of milling equipment are discussed in the chapter on plant. Rather more descriptive detail on practical manufacturing procedures would provide a better balance in this section. In this field, as in others, our dependence on American publications is indicated by the list of references for further reading, but such dependence is unfortunately due in part to language problems.

The author of a work on technology is understandably not in a position to reveal much of the specific practical knowledge in his industry. It is, however, clear from the present work that this does not prevent a fundamentally sound and informative textbook from being produced and students will be particularly grateful to the author.

I. S. Moll

Manufacturers' Publications and Pattern Cards

The Society does not accept any responsibility with regard to the statements in the following notes. Any publication abstracted may be referred to by members of the Society on application to Dr. C. B. Stevens, Dyeing Department, Leeds University

Courtaulds Ltd.

Fibro-Duracol. Available Shades and Colour Fastness— This booklet describes the ranges of mass-pigmented viscose rayon staple currently available. Twenty-two colours in three different length/denier combinations are included in the standard range while crimped staple fibre is available in thirteen colours, each in two length/denier combinations. Fastness data are given based on assessments made according to the Third Report of the Society of Dyers and Colourists Fastness Tests Co-ordinating Committee, with the exception of fastness to the "carrier" technique, and hypochlorite, enzyme desizing, solvent spotting, wet Fadeometer and weathering, for which details are given.

Farbwerke Hoechst A.G.

Variogen Base I— Provisional Leaflet VM2 describes the application of the first member of a new range of diazo components which give insoluble azo dyes capable of conversion into metal complexes by treatment with copper or cobalt salts. Thus with Variogen Base I the azoic combinations based on arylamides of 2,3-hydroxynaphthoic acid give greens when complexed with cobalt and blue-greys with copper. With Naphtol AS–LB dark greys are obtained with cobalt and dark blues with copper. With Naphtol AS–GR greens are obtained with copper. The metal complexes may be formed on the fibre by either of two methods. (1) By treating the azoic dyeing in a conventional hot alkaline solution of a non-ionic detergent containing the appropriate heavy metal salt and an alkali-stable complex builder such as Trilon A or B. This method gives the brighter colours. However, it is necessary to ensure complete removal of metal-salt residues to obtain maximum fastness to rubbing and a further treatment in a hot alkaline solution of detergent plus sequestering agent may be necessary to achieve this. (2) By incorporating the metal salt in the diazo solution, allowing coupling to proceed at 50–60°C. at pH 5–5·7 for 20 min. and then raising the solution to the boil and continuing the treatment for 30 min. when metallisation is complete. Aftertreatment in a boiling alkaline solution of detergent and sequestering agent (Trilon B) completes the process. This method gives less bright dyeings but their fastness to dry and wet rubbing is excellent. It is sometimes also quicker and cheaper. Solutions of diazotised Variogen Base I are stable in presence of cobalt salts which may be added during diazotisation but copper salts should not be added until coupling is well advanced. Each azoic combination has an optimum pH range within which metallisation occurs more readily and pH control is thus required. Dark violets are obtainable using nickel salts in the same way, but these are of limited interest. The unmetallised azoic dyeings are dischargeable to white and by subsequent metallisation at the boil white and coloured discharges on very fast grounds can be obtained. Fastness data are given for dyeings on cotton of twenty-four different Variogen Base I–Naphtol combinations metallised with cobalt salts and a further twenty-two metallised with copper salts. Dyeings metallised with copper can be resin-finished since this has little or no effect on hue, but the cobalt complexes undergo significant colour change and such finishing is not recommended. A selection of green and grey dyeings has been submitted for approval for the "Indanthren" fastness label.

Imperial Chemical Industries Ltd.

Technical Information Leaflets— *Dyehouse No. 550 (Replaces No. 500)*— Subject Index to Technical Information Leaflets (Dyehouse) Nos. 161–549.

Dyehouse No. 556. Pigments: Definition of Degrees of Fastness: Use of International Grey Scales and Standard Depths— The advantages of using the International Grey Scales for assessing the effect of exposure to the particular agency on the coloured pattern material or contact staining of secondary test material on bleeding into the reagent are stressed. Fastness to weathering cannot be covered precisely by using these scales but it is intended that additional information shall be provided on the changes which occur related to the contract ratings of the *Grey Scale for Assessing Change in Colour*. The importance of "standard depths" for testing is stressed and a selection of the internationally accepted standard depths for textile testing is recommended, viz. self-shade and 1/3, 1/25 and 1/200 Standard Depth. Reference to these four depths will be made in future publications and the ratio of pigment to white used to give these standards will be quoted.

Dyehouse No. 557 (*Replaces No. 447*). *The Felisol Label*— The continuing expansion of the International Association for the Felisol Label (I.F.A.) is shown by the formation of two more national organisations to give a total of six. There are now twenty-three associate members in four countries and thirteen dye makers (mostly European but including American) are members. Dyes accepted by the I.F.A. now include forty-eight Brenthol–Brentamine combinations.

Dyehouse No. 558. Wool Dyes: A New Test for Assessing Level-dyeing Properties— The ability of a dye to produce a level dyeing on wool under any given conditions depends upon (*a*) its migrating power and (*b*) its rate of dyeing. The Society of Dyers and Colourists' Committee on the Dyeing Properties of Wool Dyes discussed a practical test which would integrate these two factors but did not recommend an approved test. The test described in this report has now been modified to meet the pressing need for a test which is capable of being assessed using the *Grey Scale for Assessing the Effect on the Pattern*. Full details for carrying out the test are given. The recommended depth of dyeing is the I.S.O. standard depth. Using this test level-dyeing assessments are given for ranges of Carbolan and Coomassie dyes applied by the Carbolan Salt A method in 1/1 standard depth, together with average assessment figures (arbitrary) recorded by experienced wool dyers and based on practical experience. Photographs of sets of dyeings obtained with dyes that give assessments of 1, 3 and 5 are also included.

Dyehouse No. 561 (*Replaces No. 524*). *Procion/Soledon Combinations in Dyeing: Production of Yellow–Green Shades on Cotton and Viscose Rayon Fabrics*— In addition to the information given in *T.I. No. 524*, details are given of a pad–jig development method for producing a green on spun viscose rayon cloth.

Dyehouse No. 562. Printing of Acrylic–Cellulosic Fibre Unions— Prints of good fastness to light and wet treatments and good solidity are obtained using selected Caledon and Durindone vat dyes applied by the conventional alkali-carbonate-sulphoxylate formaldehyde (all-in) recipe. Careful selection of dyes and thorough washing-off after steaming are very important to ensure maximum fastness to rubbing. Thus treatment at 90°C. in a solution containing 5 ml. hydrogen peroxide (20 ml.) and 3 ml. ammonia (0·880) per litre, followed by soaping at the boil for 5–10 min., is recommended.

Pigments for Automobile Finishes— This card describes seven pigments possessing the very high fastness to heat, light, and solvents essential for car finishes. Each pigment is represented by four patterns illustrating typical usages at various degrees of reduction using rutile titanium dioxide as the white pigment and also aluminium paste in a standard aluminium finish.

Monolite Fast Red LFDS Paste— This is an aqueous dispersion of a bright red organic pigment intended primarily for colouring polyvinyl acetate, styrene–butadiene and acrylic latex emulsion paints. It corresponds to Monolite Fast Red LFS and gives colours of high fastness to light and weathering even in pale depths.

Procion Rubine HB— This homogeneous reactive dye gives bluish-reds of good fastness to light and washing on cellulosic fibres. Dyeings are yellower and a little brighter in hue than those obtained using Procion Rubine H2B and it is more soluble and less prone to reduction. Since it is a copper complex it is not recommended for vulcanising and the use of metal-sequestering agents in the dyebath must be avoided. Fastness figures on cotton include— Light (xenon arc) 6, washing (Test No. 5, 5 times at 100°C.) 4, soda boil/hypochlorite bleaching 3.

Procion Yellow GR— This reactive dye gives full bright golden-yellows when printed on cellulosic fibres. It is suitable for application by both steaming and non-steaming processes. Fastness figures on cotton include— Light (Bombay) 5–6, washing (Test No. 5, 5 times at 100°C.) 5, hypochlorite ("dry-chemicking") 5.

Reprints—

Behaviour of Selected Derivatives of p-Phenylenediamine in Rubber Compounds— E. R. Thornley and J. T. Watts. Proceedings of the International Rubber Conference, Washington, D.C., November 1959.

New Proportioning Apparatus Improves Efficiency of Padding Process— *The Dyer*, **123** (Feb., 1960).

Sandoz A.G.

Pad–Roll Dyeings with Cuprofix C Dyestuffs on Cotton and Rayon— This card contains dyeings in two depths on cotton cloth and spun rayon cloth of fifteen Cuprofix C direct dyes which have been found particularly suitable for Pad–Roll application. Addition to the padding liquor of up to 100 g./litre of urea and of 1–3 g./litre of sodium pyrophosphate is recommended (except with Bordeaux C-3BL). Aftertreatment with 1–3% of copper sulphate/acetic acid or Cuprofix SL can be carried out on the jig, winch or padding mangle. Deep dyeings must be well rinsed to avoid poor rubbing fastness.

Selected Acid and Direct Dyestuffs for the Level Dyeing of Polyamide Fibres of Irregular Affinity by the Lyogen P Process— This card contains dyeings on cloth woven from Ban-Lon yarn of twenty-six selected acid and direct dyes. These are divided into Group A (fifteen) suitable for self colours of medium to full depth, and Group B (eleven) suitable for self-colours and in combination of any depth. Using the anionic levelling agent, Lyogen P, level dyeings may be obtained on materials differing in dyeing behaviour due to physical variations in the fibres. In particular these dyes give level dyeings on materials made from crimped fibres, e.g. Helanca and Ban-Lon yarns, and the wet fastness obtained is much higher than that obtainable with disperse dyes. They are also of interest, applied by this method, on continuous-filament nylon but, since the coverage of barriness in such continuous-filament material is more difficult, preliminary laboratory trials are advisable. Good stability to heat-setting and resin-finishing are further advantages of these dyes.

Solar Dyestuffs on Paper— This card contains colourings on bleached sulphite cellulose RKN–15 of forty-four Solar direct dyes. In addition two sets of colourings are included of six of these dyes, plus ten mixtures of them, in which the paper has been sized either before or after dyeing to demonstrate the stability of this group to sizing and the freedom from mottling. With the exception of the Solar Turquoise Blues, these dyes possess high affinity for cellulose and no special measures need to be taken to promote fixation. The fastness of the colourings to light depends upon the substrate, finishes containing mechanical wood pulp being poor in this respect. Further, the order of additions to the finish is important, addition of dye after sizing resulting in lower light fastness. Normally, sized papers show better light fastness than unsized materials.

Solar 3L Dyestuffs— This card contains dyeings in two depths on cotton and spun viscose rayon cloth of twelve Solar direct dyes characterised by very good fastness to light. These include all the "3L" dyes plus Solar Blue FGL and Solar Red Brown 2RL which approach the light fastness standard of "3L" range. These dyes are particularly recommended for dyeing dress materials, linings, and furnishings and, with the exception of Green 3LB, rainwear. Suitability for continuous and semi-continuous application is indicated as is also aftertreatment with Cuprofix SL to improve fastness to wet treatments with only a very slight reduction in fastness to light. The minimum fastness to light of the "3L" range in standard depth on cotton is 7.

Ceranine PN— A cationic softening agent recommended for use on polyacrylonitrile fibres, particularly high-bulk yarns, and also of interest on many other fibres.

LEUCOPHOR A— This fluorescent brightening agent is primarily intended for use on cellulosic fibres to give brilliant whites, slightly bluish in tone. Its stability to light is as good as can be expected with this type of product and it has the advantage that the products of photodegradation are colourless. It has good stability to acids and to heat and is thus useful in acid scrooping and in resin-finishing using acid catalysts. It is compatible with cationic agents, particularly softeners.

Sandoz Products Ltd.

ALIZARINE LIGHT BLUE FBLL— This equalising acid dye gives bright blues on wool. It is characterised by very good levelling properties and dyeings have very good fastness to light, carbonising, and salt water spotting. It is thus particularly suitable for dyeing carpet yarns, hosiery yarns, and ladies' dress materials, alone and in combination with Azo Rubinole 2G and Xylene Light Yellow 2G for a wide range of fashion colours, and with Azo Rubinole 3GP and Xylene Light Yellow 2GP, where fastness to perspiration is required. Cellulosic fibres and secondary cellulose acetate are reserved white. Fastness figures include— Light 5–6, salt water spotting 4–5, carbonising 4.

ARTISIL DYES ON COURTELLE KNITTED FABRIC— This card contains dyeings in two depths on Courtelle knitted cloth of sixteen disperse dyes and a further three are shown dyed to a pale depth only. It is emphasised that the saturation point of the fibre for a given dye must not be exceeded or reduction in fastness to light and wet fastness results and this class of dye is limited to producing light to medium depth dyeings. So used, they are extremely level dyeing and exhibit high fastness to light and very good fastness to other agencies. Thus, the fastness to daylight in 1/25 standard depth is 6 or better (in all cases except two) and to washing (ECE, 60°C.) 5 (loss in depth and staining of adjacent Courtelle), 4–5 or better (staining of adjacent wool).

Abstracts from British and Foreign Journals and Patents

The titles of abstracts may be modified. Abbreviations of names of firms are listed in J.S.D.C., **68**, *23 (Jan. 1952), and also, together with symbols and the periodicals abstracted, in the annual index*

I— PLANT; MACHINERY; BUILDINGS

Vacuum Dyeing Apparatus

N. D. Il'yashuk *Tekstil. prom.*, **19** (Oct 1959) 57–59

Apparatus for dyeing of hosiery and made-up articles (cotton, viscose, cuprammonium, wool, 6-nylon) under vacuum with direct, sulphur, vat, and acid dyes, and for scouring and peroxide bleaching is described. Dyeing is carried out at a liquor ratio of 15 : 1 under 70 mm. pressure for 70–80 min. in a rotating drum. Advantages claimed are considerable reduction in time of dyeing, and economy in steam (85·7%), dye (20%), and wetting agent (80%). A diagram of the apparatus is given. G.J.K.

PATENTS

Carbon Black Furnace Dual Fluid Injector

Phillips Petroleum Co. *BP* 834,457 (U.S.A. 6 Feb 1956)

Dyeing Synthetic Fibre Tow

Abbott Machine Co. *USP* 2,906,593 (14 March 1957)

Machine for dyeing 250–300 lb. of tow wound on bobbins each holding 20 lb. of tow. It enables the tow to be dyed before it is heat stretched and made into tops. C.O.C.

Winding and Unwinding of Cloth and the like on Rollers

Benteler-Werke *BP* 834,388 (Germany 18 June 1957)

Rollers on which the cloth is wound are movable to and from a winding position, an unwinding position, and an intermediate position. It is first wound in a single layer on to a roller in the winding position. The full roller is then moved to the unwinding position while an empty roller is moved from the intermediate to the winding position. Then the cloth is wound in double layers on to the empty roller, one layer being taken from the full roller and the other from a length of cloth fed in for winding. The apparatus is compact and there is no need to fold the cloth. The cloth can be wound to any desired length so that it can be treated with reagents in the chamber containing the apparatus for any desired time. C.O.C.

Maintaining a Web along a Predetermined Path

Dynamit *BP* 834,014 (Germany 29 June 1955)

Treating One Surface of a Moving Web with Liquid

National Vulcanised Fibre Co. *BP* 834,255 (U.S.A. 2 Nov 1955)

Apparatus in which the liquid is applied without either surface of the web being mechanically contacted during the application. C.O.C.

Treating Fibrous Materials with Liquids

National Research Development Corpn. *BP* 834,403 (9 March 1955)

Hides, cloth, etc., are rigidly supported in the bath and a succession of liquid-disturbing members are moved close to the hides, etc., at a speed sufficiently high to induce cavitation. The cavitation bubbles caused collapse in contact with the material and so cause ultrasonic irradiation within it. C.O.C.

Drying Chamber

Tomlinsons (Rochdale) *BP* 834,589 (6 Dec 1956)

A drying chamber which is readily and quickly assembled and needs no supporting framework of angle irons assembling before the insulation panels are placed in position. C.O.C.

Drying Webs

Hall & Kay *BP* 834,638 (6 June 1958)

A drying cylinder has externally-mounted longitudinal channels having openings leading into the cylinder. A baffle of more than semicircular cross-section in the cylinder has sealed edges to seal all the openings covered by it and leave the remainder open. One end of the cylinder is closed and the other connected to an air extractor. C.O.C.

Spreading Thick Viscous Media

Rubber Improvement *BP* 834,413 (11 April 1956)

A thick viscous medium, e.g. poly(vinyl chloride) paste, is fed under externally applied pressure from a rigid container. The underside of the bottom wall of the container is formed as a spreading member, the medium being fed from an aperture in this wall on to the substrate. C.O.C.

Screen Printing Machine

Colden Manufacturing Co. *BP* 834,582 (15 Aug 1956)

In a machine where the cloth to be printed is carried on an endless belt beneath the stencils, the belt is moved intermittently by pusher members reciprocating in the direction of travel of the belt. These pushers coact with individually longitudinally adjustable abutments placed at intervals along each edge of the belt. This allows adjustment of the mechanism to compensate for stretch or shrinkage of the belt in different portions of it. C.O.C.

Printing on the Tips of Pleats of Pleated Fabrics

United Merchants & Manufacturers *BP* 835,360 (U.S.A. 6 Dec 1957)

A machine which enables multi-coloured printing of the tips of the pleats. C.O.C.

Electrostatic Spraying Installation

Licentia Patent-Verwaltungs *BP* 834,275 (Germany, 28 Nov 1955)

Modification of *BP* 776,245. The spraying material is kept circulating all the time in its container so that it is always available at the spraying gap in the same fluid condition. C.O.C.

Electrostatic Spray Coating with Compositions Containing Fusible Materials

Harper J. Ransburg Co. *BP* 833,996 (U.S.A. 7 Feb 1955)

Calendering Synthetic Resins
Montecatini Societa Generale per l'Industria Mineraria e Chimica *BP* 834,509 (Italy 29 March 1957)

Apparatus for the continuous calendering of synthetic resins comprises two calendering rollers rotatable at different speeds, and at least two pairs of disc-shaped knives. These knives are resiliently mounted for free rotation above the driving roller on which a sheet of resin is formed. The edges of the knives are urged into contact with the surface of the roller at points lying on two different lines one on either side of a line on its top surface vertically above the axis. The pairs of knives are at opposite ends of a central portion of the roller corresponding to a central feed portion of the nip between the calendering rollers. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7) (IV p. 516)
Dyeing Textiles on Forms (VIII p. 520)
The Electro-fixer, its Design and Possibilities of Application (IX p. 520)
The Padding Mangle (X p. 522)

III— CHEMICALS; AUXILIARY PRODUCTS; FINISHING MATERIALS

Constitution and Properties of Surfactants. II— Sorption of Anionic Surfactants on Fibres
H. Kölbel and H. Hörig *Angew. Chem.* **71** (1959) 691–697
Chem. Abs., **54** (10 April 1960) 7159

Determination of the sorption of members of the homologous series of Na alkyl sulphates, alkyl sulphuric acids, Na soaps and *p*-alkylbenzenesulphonic acids showed that sorption was of single ions rather than micelles and was much more influenced by the nature of the fibre than by that of the surfactant. Three classes of fibres were used: (1) fibres, e.g. polyacrylonitriles and polyesters, which soil mainly by dispersion forces, (2) fibres, e.g. cellulose, having OH or NH groups capable of H bonding, and (3) fibres, e.g. wool and polyamides, having NH_2 groups which form positive ions in acid solution. Class 3 fibres differ from those of class 2 in sorbing much more strongly in acid than in neutral solution. Dispersion forces, active with all three classes, hold alkyl chains parallel to the fibre surface. As these forces increase with the number of electrons, sorption should increase with chain length of the sorbate. This is true of class 1 fibres but with the other two fibres one or two maxima occurred as the sorbate chain was lengthened. Decreased sorption following these maxima seems to be caused by extension of the hydrocarbon chain of a molecule sorbed in one of the regularly spaced functional groups of the fibre blocking the next one or two sorptively active sites. C.O.C.

Aldehyde-Ethyleneimine Reaction Products as Finishes for Cotton Fabrics
L. H. Chance, R. M. Perkins, and W. A. Reeves
Text. Research J., **30** (April 1960) 305–311

Evaluation as wash-and-wear finishes for cotton of the reaction products of ethyleneimine with glyoxal, glutaraldehyde, acrolein, and crotonaldehyde respectively. The acrolein–ethyleneimine product imparted good crease recovery properties to cotton cloth. 19 references. C.O.C.

Relationship between Chemical Structure and Fungicidal Activity
D. Woodcock *Plant Pathol., Problems progr.*, **1908–1958**, 267–279 (Feb 1959)
Chem. Abs., **54** (10 April 1960) 7044

Review, 110 references. C.O.C.

Carragheenates and their use in Textile Printing
H. Schulzen *Melliand Textilber.*, **41** (May 1960) 596–600

Preparation and purification of the carragheenates from carragheen moss is described and the chemical constitution of the compounds occurring in the moss is discussed. Properties of carragheenate solutions are compared with those of alginates. W.M.

PATENTS

Alkylcarbamylalkane Sulphonates for preventing Coagulation of Lime Soaps
Unilever *BP* 834,225 (14 Oct 1955)

Compounds of formula $R^1R^2N{\cdot}CO{\cdot}R^3{\cdot}SO_3X$ (R^1 = Alk of 10–18 C; R^2 = H, Alk of 4 C or hydroxyalkyl of 1–4 C; R^3 = alkylene of 1–3 C; X = alkali metal, NH_4 or substituted NH_4), e.g. Na dodecylcarbamylmethane sulphonate, added to soap prevent coagulation of any lime soaps formed when the soap is used in hard water. C.O.C.

Warp Size
Monsanto Chemical Co. *USP* 2,909,447 (8 Feb 1952)

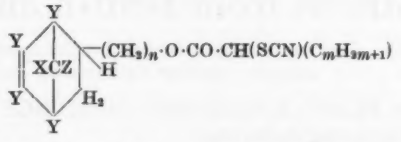
The alkali metal salts of low-mol.wt. copolymers of 90–98 mol.% of vinyl acetate and 10–2 mol.% of an unsaturated organic compound of 3–9 C and containing at least 1 carboxylic group, e.g. crotonic acid, are excellent sizes for warps with the exception of those of nylon. C.O.C.

Starch Cross-linked with Hexahydro-1,3,5-triacryloyl-s-triazine
Chas. A. Krause Milling Co. *USP* 2,910,467 (18 Jan 1956)

Heating starch with an aqueous solution of hexahydro-1,3,5-triacryloyl-s-triazine yields adhesives and binding agents of extreme resistance to shear, heat or high alkalinity. They can be produced so as to have, if desired, very high viscosity. C.O.C.

Fungicides and Bactericides
Velsicol Chemical Corpn. *USP* 2,909,458 (1 July 1957)

Compounds of formula—



(X and Z = same or different, H, Br or Cl; Y = Br or Cl; n = 0–14; m = 0–14), e.g. 1,2,3,4,7,7-hexachloro-5-methylhydroxybicyclo(2.2.1)-2-heptene, are excellent fungicides for use on leather, etc.

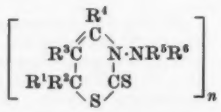
Olin Mathieson Chemical Corpn. *USP* 2,909,459 (22 May 1956)

Compounds of formula—

(R = H, Alk, alkoxy, halogenoalkyl) and their alkali and metal salts and their derivatives, e.g. the disulphide, have their fungicidal and bactericidal effectiveness much prolonged when in contact with proteinaceous material if a small amount of a soluble borate is also present.

Monsanto *USP* 2,909,460 (21 March 1957)

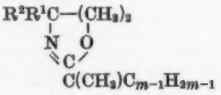
Compounds of formula—



(R^6 = hydrocarbon of 1–12 C free from non-benzenoid unsaturation; R^1, R^2, R^3, R^4, and R^5 = same or different H or R^6; n = 1 or 2), obtained by condensing an $\alpha\beta$-olefinic carboxyl compound with a salt of a 3-hydrocarbon- or 3,3-dihydrocarbon-substituted dithiocarbazic acid in presence of acid, have strong fungicidal action. C.O.C.

Oxazoline and Oxazine Derivatives as Antiseptics and their Polymers and Copolymers as Auxiliary Agents
Rohm & Haas Co *BP* 834,308 (U.S.A. 11 May 1956)

Compounds of formula—



(R^1 = CH_3; R^2 = Alk of < 9 C; or R^1 and R^2 together = a divalent satd. aliphatic hydrocarbon of 4–9 C and together with the C atom of the ring form a 5- or 6-membered carbocycle; m = 1 or 2; n = 1 or 2) have in many cases good antiseptic properties, e.g. 2-vinyl-4,4-dimethyl-5,6-dihydro-4H-1,3-oxazine is used for the mildewproofing of leather and textiles. They are readily polymerised and

their polymers and copolymers are useful in coating compositions, in finishing textiles and paper, etc. C.O.C.

Polymers of Quaternary Ammonium Compounds
Rohm & Haas Co. *BP* 834,410 (U.S.A. 21 March 1955)

Describes production of homo- and co-polymers comprising units having a branch containing quaternary ammonium nitrogen to which is attached a radical containing carbonamido or ureido groups. They are soluble or readily dispersed in water but presence of the carbonamido and ureido groups enables them to be insolubilised. They have an extremely wide field of uses depending on the monomers chosen. C.O.C.

Fungicides
Gy *BP* 834,576 (Switzerland 22 July 1955)

Amides of salicylic acid and their derivatives having halogen substituted in the benzene ring derived from aliphatic and alicyclic primary amines of 3–6 C are more powerful fungicides than the corresponding aromatic amines. This property is particularly marked in the protection of cotton against mildew. Thus salicylic acid-*n*-amylamide applied as a 0·1% solution in ethylene glycol monomethyl ether to cotton (100% pickup) gives good protection against mildew spots and rot. C.O.C.

Silicone Water-repellent Composition
General Electric Co. *BP* 834,376 (U.S.A. 13 May 1957)

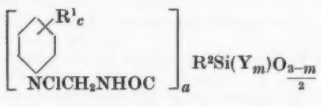
Textiles and other porous materials are rendered water-repellent by use of a composition comprising, by weight, (1) 10–60% of a compound of formula $Ti(OR)_4$ (R = aliphatic hydrocarbon of < 12 C which may be hydroxylated or aminated so long as it contains < 4 OH), (2) 25–75% of a methylpolysiloxane copolymer made up mainly of siloxy and SiO_2 units, the ratio of CH_3 to Si being 1 : 1–1·25 : 1, and (3) 10–50% of a liquid of formula $R_nSiO_{(4-n)/2}$ (R = same or different, Alk or chlorinated phenyl (3–5 Cl per C_6H_5), the chlorinated phenyl radicals being 5–25% of the total Alk and chlorophenyl radicals; n = < 2·5 and on average 1·96) and viscosity 10–100,000 cs. at 25°C. C.O.C.

Salts of Polyamine Polyepoxide Adducts as Curing Agents for Polyepoxides
Shell Development Co. *USP* 2,909,448 (7 March 1955)

The salts of acids with soluble adducts of polyamides and polyepoxides, e.g. of diethylene triamine and a diglycidyl ether of 2,2-bis-(4-hydroxyphenyl)propane, are effective catalysts for the curing of fabrics, particularly those containing wool, which have been impregnated with polyepoxides to reduce their tendency to shrink and to improve their water repellency. C.O.C.

Siloxanes for Treating Textiles
Midland Silicones *BP* 835,516 (U.S.A. 29 May 1957)

Compounds of formula—



(R^1 = aliphatic hydrocarbon of < 4 C; c = 0, 1, 2 or 3; a = 1 or 2; R^2 = di- or tri-valent satd. aliphatic or cycloaliphatic hydrocarbon of > 1 C; Y = monovalent or fluorinated hydrocarbon; m = 0, 1 or 2) are especially suitable for producing fast-to-washing finishes on cellulose fabric and for use as fixing agents for conventional organopolysiloxanes on textiles. C.O.C.

Pigmented Silicone Water-repellent Finishes
Union Chimique Belge *BP* 834,962 (Belgium 8 April 1957)

Silicone compositions containing a thermoplastic resin give improved water-repellency if a finely divided pigment, e.g. metal oxides, sulphides or sulphates or metal powder, is added to them. They are applicable to porous asbestos cement sheet, porous tiles, tarred felt, etc. C.O.C.

Chromium Co-ordination Complexes
Minnesota Mining & Manufacturing Co. *USP* 2,909,545 (11 March 1955)

Perchlorofluoromonocarboxylic acids of 4–20 C are treated with trivalent Cr compounds which are at least one-third basic, e.g. chromic chloride or chromyl chloride which is reduced during the reaction to an oxygen-containing trivalent Cr compound, to form the complexes. When the complexes are used as water-repellent agents the chromyl halogen must be hydrolysed just before or during application of the complexes to the material to be rendered water-repellent. C.O.C.

Fibrous Structures Impregnated with Synthetic Resins
DuP *BP* 833,679 (U.S.A. 21 July 1955)

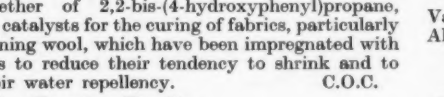
The product obtained by polymerising a mixture of (*a*) acrylonitrile, (*b*) an α-olefinic carboxylic acid, and (*c*) an α-olefinic carboxylic ester of a satd. aliphatic monohydric alcohol of 1–12 C has varied uses, e.g. as a binding agent in producing bonded fibre fabrics, for coating or impregnating paper, etc. The ratio by wt. of (*a*) to (*b*) is from 20 : 80 to 85 : 15 and (*b*) is 1·5–15·0% of the total monomer mixture. C.O.C.

Substituted *NN'*-Diphenylsulphamides — Mothproofing Agents
Gy *BP* 833,788 (Switzerland 18 May 1956)

Compounds of formula $A^1R^1N{\cdot}SO_2{\cdot}NA^2R^2$ (R^1 and R^2 = H or Alk of < 6 C; A^1 and A^2 = phenyl substituted by Hal or CF_3 so that they contain > 3 Hal) give excellent protection to wool against insect pests. Thus wool treated with 4% of its weight of *NN'*-bis-(3-trifluoromethyl-4-chlorophenyl)-sulphamide in aqueous solution for 30 min. at 40°c. is mothproof. C.O.C.

Polyglycol Ether Derivatives as Softening Agents
Ciba *BP* 833,748 (Switzerland 15 July 1955)

Compounds of formula—



(n and m = same or different, 2, 3 or 4; R = aliphatic hydrocarbon; –OCR is of > 19 C; k = whole number), e.g. the product obtained by diacylating diethylenetriamine in stearic acid and condensing with ethylene oxide, are softening agents for viscose rayon. C.O.C.

Sizing Composition for Garments
R. A. Hatcher *USP* 2,907,676 (14 Nov 1956)

A mixture of a water-soluble sugar syrup and alcohol is used preferably together with glycerin and a wax. It exhausts from hydrocarbon solvents on to the garments. C.O.C.

Vat or Sulphur Dyeing (VIII p. 520)
Alginic Acid Derivatives as Fire Resisting Agents (X p. 522)

IV— RAW MATERIALS; INTERMEDIATES; COLOURING MATTERS

Thermochromism of Two Disulphides
R. E. Davies and C. Perrin
J. Amer. Chem. Soc., **82** (5 April 1960) 1590–1594

Thermochromism of 2,2'-dibenzthiazolyl disulphide and tetramethylthiuram disulphide (I), both used as accelerators in vulcanising rubber, has been observed in homogeneous soln. over the temp. range 25–100°c. Beer's law holds for both cpd. at 25°c. and 100°c. indicating no reversible dissociation. Thermochromism is due to thermal broadening of absorption band caused by increased population of higher vibrational states of the ground state. Radical dissociation is discounted since resultant optical density is higher than that calculated from the concn. of radicals produced in the experiment time. Mode of radical decomposition of (I) with formation of elemental sulphur is discussed and clarified by use of thermodynamic and quantum mechanical criteria. F.J.

Ultraviolet Absorption Spectra of α-Nitroso-β-naphthol and Its Copper Chelate
K. K. Chatterjee *Anal. Chem. Acta*, **20** (1959) 423–427
Chem. Abs., **54** (25 March 1960) 5589

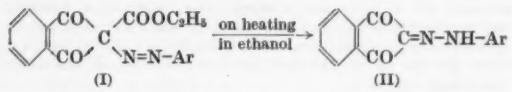
Comparative study of the ultraviolet absorption spectra of α-nitroso-β-naphthol (see C.I. 10005) and of β-naphthol in neutral alcohol and in presence of 0·1 N-$HClO_4$ and 0·1 N-KOH respectively, favoured the quinone–oxime structure of α-nitroso-β-naphthol. The spectrum of the Cu (II) chelate indicates planar configuration of the complex with considerable resonance between the quinonoid and benzenoid structures of the ligand. C.O.C.

Condensation of the Sodium Salt of Ethylindandione-1,3-carboxylate-2 with Diazotised Nitroaniline

É. Yu. Gudrinietse, G. Ya. Vanag, and L. Yu. Sakhar

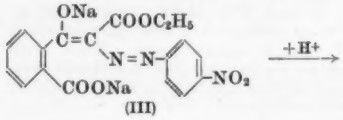
Dokladÿ Akad. Nauk S.S.S.R., **128** (21 Oct 1959) 1182–1184

Condensation of diazotised *o*-, *m*-, and *p*-nitroaniline with the sodium salt of ethylindandione-1,3-carboxylate-2 in acid soln. yields yellow arylazo compds. (I) insoluble in water, but readily sol. in methanol, ethanol, acetone, ether, glacial acetic acid, and dioxan—

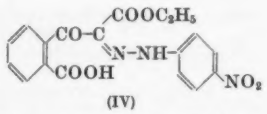


(I) (II)

(Ar = *o*-, *m*-, or *p*-$C_6H_4NO_2$). Condensation in alkaline soln. (pH ~ 8–9) also yields II. Heating of *p*-$C_6H_4NO_2$ deriv. of I with Na ethoxide in ethanol gives (III)—

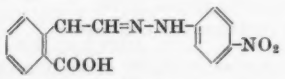


(III)



(IV)

Monoammonium, bisdiethylammonium, and dipiperidinium salts of IV have been prepared. IV is stable to hydrolysis, cleavage of the ethoxy group occurring only on prolonged boiling in a mixture of glacial acetic and sulphuric acids giving—



Preparative data are mentioned. G.J.K.

Azo Dyes from Acetoacetanilides

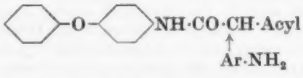
II— Monoazo Dyes from 4-Aminodiphenyl ether and 4-Aminodiphenyl sulphone

A. Arcoria

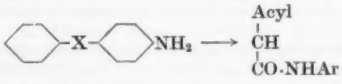
Boll. sedute accad. Gioenia sci. nat. Catania [4], **4** (1958), 304–310

Chem. Abs., **54** (10 Mar 1960) 5091

Ethyl acylacetates were heated in xylene with 4-aminodiphenyl ether to give the amides which were coupled with diazotised arylamines to give monoazo compounds—



whose m.p. and spectral characteristics were recorded, as were those of the monoazo compounds—



(X = O or SO_2).

III— Disazo Dyes from 4,4′-diaminodiphenyl ether, -diphenyl sulphide, and -diphenyl sulphone

A. Arcoria and N. Marziano

Ibid., 407–414

Chem. Abs., loc. cit.

These three diamines were tetrazotised and coupled with Acyl·CH_2·CO·NH·Ar under alkaline conditions, giving disazo dyes very similar to the monoazo dyes described in Part II.

IV— Disazo dyes from 4-Amino-4′-(*p*-aminophenoxy)diphenyl ether, -diphenylsulphide, -diphenyl sulphone, and 4-Amino-4′-(*p*-aminophenylthio)diphenyl sulphide

A. Arcoria and F. Bottino

Ibid., 415–422

Chem. Abs., loc. cit.

Similar disazo compounds were prepared from these diamines. E.S.

Effect of the Introduction of Alkyl Groups on the Dyeing Properties of Monoazo Acid Dyes

J. Meybeck, P. Ruckstuhl, and J.-M. Thumann

Teintex, **25** (April 1960) 241–279

Introduction of alkyl groups into the benzene ring in either *o*-, *m*-, or *p*-position to the azo group has no marked effect on the hue. Increasing the length of the aliphatic chain has a varying but not significant effect on the hue and on the absorption maximum. The purity of the colour is slightly lessened. Introduction of aliphatic groups decreases exhaustion equilibrium of substantive dyes, the longer the chains the greater this effect. In monoazo acid wool dyes introduction of aliphatic groups of < 9 C increases the initial rate of dyeing in acid medium. Longer chains decrease the rate of dyeing. Introduction of groups of > 7 C increases the wash fastness, in some cases very considerably. On the other hand the fastness to light decreases in some cases from C_2H_5 in other cases from 6 or 8 C onwards. The octyl group seems to be the best compromise for obtaining excellent fastness to washing together with medium or very good light fastness. The effect of long chains on affinity (of acid dyes) is small in the case of disulphonic acids in neutral medium but is of importance in the case of monosulphonic acid or for dyes having markedly hydrophobic groups. Introduction of aliphatic groups into the developer, which is a tedious operation, does not offer any advantages. The position of the sulphonic groups in the case of disulphonic acids does not seem to have any significant effect. W.M.

Effect of Organic Solvents on the State of Aggregation of Direct Dyes in Solution and on their Rates of Diffusion in Cellophane

B. N. Mel'nikov and P. V. Morÿganov

Kolloid. zhur., **21** (Sept–Oct 1959) 618–624

Diffusion coefficients of Sky Blue K, Diazo Black C, and Pure Sky Blue in presence of monoethanolamine (0–100 g. per litre), diethylamine (0–15 g.), polyvinylpyrrolidone (0–1 g.), and pyridine (0–200 g.) have been determined (25°c.) and the absorption spectra (400–750 mμ.) of these systems measured. Addition of organic solvents first causes appreciable decrease in the degree of aggregation of dye molecules but with large organic solvent content an increase in particle size of the dye, caused by increased solvation, occurs. In addition, the diffusion coefficients of these dyes at 40°c. through Cellophane membrane under stationary conditions in presence of varying amounts of the first 3 organic solvents have been tabulated; the coefficient increased on the average 3–5 fold, and in some cases 11–25 fold. G.J.K.

Structure, Hue, and Fastness to Light of Direct Polyazo Dyes

F. Filippychev

Nekotorye Voprosy Sinteza i Primeneniya Krasiteleĭ (Leningrad: Gosudarst. Nauch.-Tekh. Izdatel. Khim. Lit. 1956) 21–47

Referat. Zhur. Khim. (1957) Abstr. No. 38914

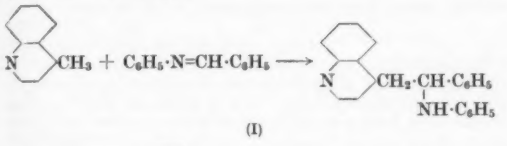
Chem. Abs., **54** (10 April 1960) 7152

Study of the relationship between structure and hue, fastness to light, and substantivity. In azo dyes containing only one conjugated azo system the colour deepens when the number of azo groups is increased to 3–4, further increase in the number of azo groups does not deepen the colour and after a certain limit is reached the colour becomes paler. The 1,4-conjugated azo system produces the strongest deepening of colour, particularly the one involving naphthalene nuclei. When all auxochromes in the molecule are included in a common conjugated system of dye with one conjugated azo system, the dye is more brilliant and has a narrower spectrum than dyes containing auxochromes outside the conjugated chain. Dyes consisting of several unseparated azo systems are usually dull and predominantly brown, grey, black or olive. In dyes containing separated conjugated azo systems, the hue is largely defined by the nature of the isolating group, the stronger its isolating properties, the nearer the dye's colour to the sum of the colours of the separate systems. If the isolating group does not completely interrupt the conjugation between the different systems, interaction takes place between them with the result that the colour of the dye is then the sum of the colours of the separate systems. In addition such polyazo dyes are less fast to light and less substantive than dyes having individually

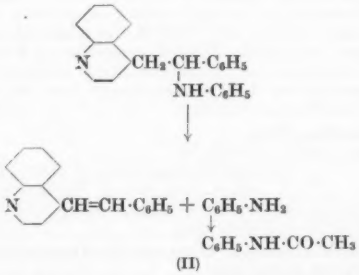
conjugated azo systems. The substantivity of 1,4-polyazo dyes is largely dependent on the number of azo groups, increasing up to 3–4 groups and decreasing above this number. Azo dyes having uninterrupted conjugated chains have higher substantivity than isomeric dyes having separated conjugated systems. The structures showing best fastness to light among the straight chain dyes are 1–4 polyazo dyes having $\geqslant 3$ azo groups, Cu complexes of azo dyes, dyes having separated conjugated systems (cyanuric ring, carbamide or other separating structures) and some condensation products of dinitrostilbene-disulphonic acid with various amino azo dyes. Direct relationship exists between the stability of dyes to tautomeric changes and fastness to light, the less the tendency to tautomeric change the better the fastness to light.
C.O.C.

Preparation of 2- and 4-Sterylquinoline by Means of Benzilidine Aniline
V. A. Izmail'skiĭ and P. A. Solodkov
Zhur. obshch. khim., **29** (Dec 1959) 3930–3934

When quinaldine or lepidine is heated under reflux with benzilidine aniline in presence of acetic anhydride, 2- or 4-sterylquinoline is produced. The reaction takes place in two stages—



(I)

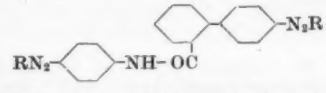


(II)

With quinaldine reaction is completed in 5 min. at 156–158°c. giving 80% yield. The reaction in butanol requires heating at 160°c. for 68 hr. and gives 54·3% yield. 4-Sterylquinoline is formed in 30 hr. at 140°c. with 67·4% yield, the yield is only 30% when the reaction time is 12 hr. Absence of acetic anhydride decreases the yield to 21%.
T.Z.W.

Effect of Steric Factors on the Properties of Dyes Containing a Diphenyl Ring. XII— Affinity for Cotton of Bisazo dyes Containing Amino Groups
B. M. Krasovitskiĭ and B. I. Ostrovskaya
Ukrain. khim. zhur., **25**, No. 4 (1959) 493–496

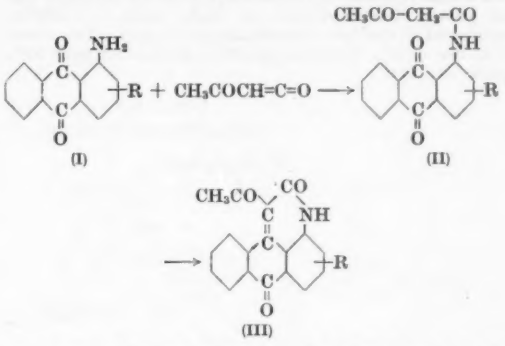
Using the method of Peters and Vickerstaff (*Proc. Roy. Soc.*, **A 192** (1948) 292) affinities (kcal./mole at 80° and 100°c.) of 25 bisazo dyes containing amino groups (AG) in the diazo component, and having an identical number of sulphonic groups, have been determined. Simultaneous occurrence of diphenyl and benzanilide groupings, accumulation of aromatic rings between AG or between azo and amino group, and increase in the number of AG, increase the affinity of these dyes for cotton. Dyes having the AG-containing residue in *o*-position to diphenyl bond, e.g.



(R = azo component) have little affinity for cotton because of steric hindrance.
G.J.K.

Reactions of Amines of the Anthraquinone Series with Diketen
N. A. Kirzner, Yuĭ Feĭ-béĭ, and B. A. Poraĭ-Koshits
Zhur. obshch. khim., **30** (March 1960) 890–896

1-Aminoanthraquinone (A) and its derivatives (I) react with diketen (D) to give II, which on strong heating or under the action of aq. alkali, are changed to III—



(I) (II) (III)

(R = CH_3, Cl, Br, SO_3H, C_6H_5, or $C_6H_4NH_2$). The basicity of I promotes formation of II. 1-Methyl-aminoanthraquinone and its derivatives react with D more readily than A and I respectively, yielding the corresponding anthrapyridones directly. II and III can be used as dyes on acetate rayon or as intermediates in the production of more complex dyes. The preparation of 19 compounds (II and III), showing their chemical and physical data, is described. Absorption spectra (300–500 mμ.) of 1-acetoacetylaminoanthraquinone; 1-acetyl-, 1-acetyl-*N*-methyl-, and 6-bromo-1-acetyl-*N*-methyl-anthrapyridone in organic solvents are given.
G.J.K.

***p,p'*-Diphenylstilbene**
E. E. Baroni and G. Bushbek
Zhur. obshch. khim., **29** (Dec 1959) 4055–4056

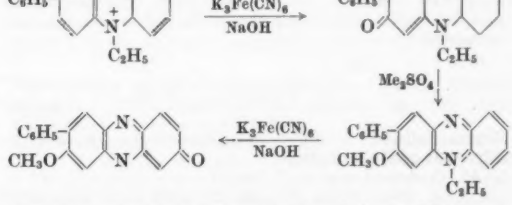
p-Phenylbenzaldehyde is condensed to *pp'*-diphenyl-benzoin by heating it in alcohol on a water bath in presence of NaCN. 90% yield is obtained. The diphenylbenzoin is mixed with Zn and alcohol and reduced by passing HCl gas and hydrogen through the mixture. A 78% yield of diphenylstilbene is claimed. *pp'*-Diphenylstilbene dissolves with difficulty in most organic solvents and is fluorescent.
T.Z.W.

Ultraviolet Absorption Spectra of 2-Methylbenzothiazole substituted in 5 and 6 Positions
M. A. Al'perovich, M. K. Grechko, and I. K. Ushenko
Zhur. obshch. khim., **29** (Dec 1959) 4045–4048

The absorption spectra of 10 derivatives of 2-methylbenzothiazole substituted in 5 or 6 positions reveal the existence of a third, intensive absorption band in the long wavelength region. Displacement of this band towards the red end of the spectrum is more pronounced in case of 6-substituted compounds.
T.Z.W.

Directional Influence of Phenyl Groups during Oxidation of Quaternary Phenazine Salts
Yu. S. Rozum
Zhur. obshch. khim., **29** (Dec 1959) 4036–4045

Oxidation of 2-phenyl-10-ethylphenazine with alkaline $K_3Fe(CN)_6$ takes place according to the scheme—

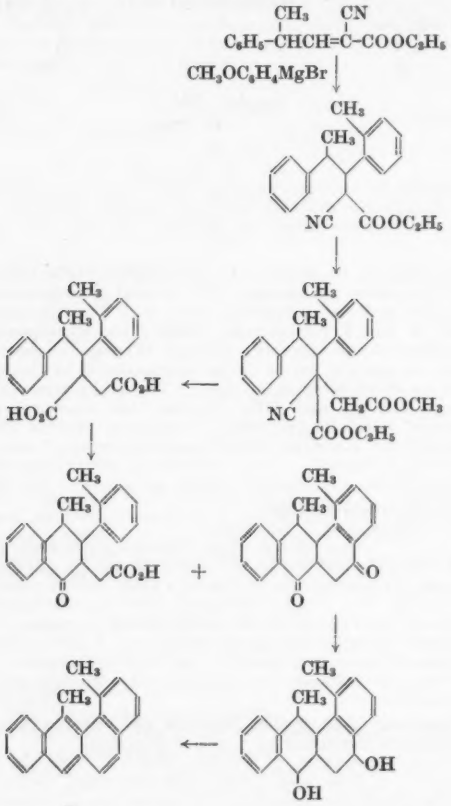


Absence of phenyl substituent in the nucleus inhibits ease of oxidation. The same applies to 1-phenyl-10-ethyl-phenazine except that the unsubstituted nucleus is more inert. Attempts to photo-oxidise the quaternary phenyl-phenazine salts failed.
T.Z.W.

Synthesis of 1′,9-Dimethyl-1,2-benzanthracene
M. S. Newman, W. C. Sagar, and M. V. George
J. Amer. Chem. Soc., **82** (5 May 1960) 2376–2379

Synthesis of pure (> 99·2%) 1′,9-dimethyl-1,2-benz-anthracene (I) by steps shown below is described.

Previous preparation of (I) consisted of (I) and 1′-methyl-1,2-benzanthracene in unknown proportions probably due to partial dimethylation at high temp. (> 300°c.) employed in the last (dehydrogenation) step. Treatment with one equiv. of sulphur at 200°c. for one hr. gave 69% yield of (I)—



(I)

F.J.

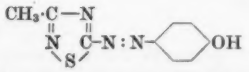
1,2,4-Thiadiazoles. X— Structure and Chemical Behaviour of 5-Nitrosamino-1,2,4-thiadiazoles; a Contribution to Heterocyclic Diazochemistry

J. Goerdeler and K. Deselaers

Chem. Ber., **91** (1958) 1025–1036

Chem. Abs., **54** (10 March 1960) 4548

Various 3-substituted-5-amino-1,2,4-thiadiazoles were treated in $NaNO_2$ + aq. H_2SO_4 or in $NaNO_2$ + acetic acid to give the corresponding 5-nitrosamino compounds which with alkalis form salts which react as isodiazotates, and with phenols and naphthols give monoazo compounds. Thus the 3-methyl compound, after treatment with acidified $NaNO_2$, gives with phenol the red-brown monoazo compound—



E.S.

Benzacridines. IV— 6,6-Dimethyl-11-keto-6,11-dihydrobenz[b]acridans

N. H. Cromwell and J. C. David

J. Amer. Chem. Soc., **82** (20 April 1960) 2046–2050

Catalytic hydrogenation and reaction with phenylmagnesium bromide converted 6,6-dimethyl-11-keto-6,11-dihydrobenz[b]acridine (I) into 6,6-dimethyl-11-keto-6,11-dihydrobenz[b]acridan (II) and 6,6-dimethyl-11-keto-12-phenyl-6,11-dihydrobenz[b]acridan (III) respectively. Dehydrogenation of (II) re-formed (I) while (III) gave corresponding 12-phenyl deriv. Absorption spectra studies of (II) and (III) showed characteristics of β-amino-α,β-unsaturated ketones, e.g. 1-phenyl-3-anilino-2-butene-1-one. F.J.

Studies on Some Thioindigoids and Related Compounds

Part I

S. K. Guha and J. N. Chatterjea

Chem. Ber., **92** (1959) 2768–2771

A series of subst. 1-acenaphthenyl-5-bromo-2-thianaphthenylindigo dyes was prepared and light absorptions compared with 5-CH_3, 5-Cl, and 5-I analogues. Thus, acenaphthenequinone (I) and 5-bromo-3-hydroxythianaphthene (II) were condensed in glacial acetic acid in presence of HCl to give 1′-acenaphthenyl-5-bromo-2-thianaphthenylindigo (III) (dyeing cotton violet-red from a deep violet vat). Similarly from derivatives of I and II were prepared the following derivatives of III (colour of alkaline vat and colour on cotton), 6′-Cl (violet, red), 6′-Br (blue, deep red) and 8′-OCH_3 (blue-violet, light violet). Aceanthrenequinone and II gave 7′,8′-benzo-III (yellow, reddish-brown). II and benzene in alcohol in presence of HCl gave 5-bromo-3-oxo-2-benzylidene-2,3-dihydrothianaphthene, and similarly its *p*-nitrobenzylidene and 4-dimethylamino benzylidene analogues. The absorption maximum shifted towards longer wavelengths in order of 5-subst. CH_3 < Cl < Br < I.

Part II

S. K. Guha, J. N. Chatterjea, and A. K. Mitra

Ibid., 2771–2774

Chem. Abs., **54** (10 April 1960) 6681

Related to the above were a series of vat dyes from the condensation of 3-hydroxy-5-methoxythianaphthene (I) and acenaphthenequinone. I was obtained from a series of reactions from *p*-anisidine and in similar manner to the above (Part I) were obtained 1′-acenaphthenyl-5-methoxy-2-thianaphthylindigo (reddish-violet on cotton) and its 6′-Br (reddish-violet) and 8′-OCH_3 (pinkish-red) derivatives, and 5-methoxy-3-oxo-2-benzylidene-2,3-dihydrothianaphthene and its *p*-nitrobenzylidene analogue. The 5-OCH_3 derivatives dyed cotton deeper than the 5-CH_3, 5-Cl, 5-Br, and 5-I analogues. A.T.P.

Phenothiazine Dyes

R. Wizinger and H. Rembold

Chimia (Switzerland), **13** (1959) 156–158

Chem. Abs., **54** (25 March 1960) 6131

Study of the bathochromic effects created by –S– and –O– bridging in dye molecules. C.O.C.

Further Spectroscopic Data on the Deep Colour of 9-Substituted Acridines

V. Zankev and A. Reichel

Z. Elektrochem., **63** (1959) 1133–1140

Chem. Abs., **54** (25 March 1960) 5243

Absorption and fluorescence polarisation spectra of a series of 9-subst. acridines (I) (substituents: H, C_6H_5, *p*-$CH_3C_6H_4$, CH_3, C_2H_5, C_3H_7, CH:CH_2, C_6H_5CH:CH, *p*-dimethylaniline, *p*-$(CH_3)_2NC_6H_4$CH:CH, $(CH_3)_2$NCH:CH, *o*-, *m*-, and *p*-$NH_2C_6H_4$CH:CH; *o*-, *m*-, and *p*-CH_3O-C_6H_4CH:CH, *o*-HOC_6H_4CH:CH; and *o*-, *m*-, and *p*-$O_2NC_6H_4$CH:CH) were determined at — 183°c. in 10^{-4} M-soln. in alcohol–ether mixtures, and the electronic transitions classified. Unsatd. aliphatic or aromatic substituents in I do not greatly influence the spectra of acridine. Combination of unsatd. aliphatic and aromatic substituents with the electron donor groups NH_2, $N(CH_3)_2$, OH, OCH_3 in *o*-, *o*- or *p*-position relative to the point of attachment of the acridine leads to a new long-wavelength band (except in *o*-HOC_6H_4-I) which depends on the strength of the donor. In aromatic substituents there is, in addition, a further new band in the middle ultraviolet in such compounds, usually in the place where acridine had a minimum. No such long-wavelength band occurs when the electron-donating substituent is in the *meta* position. Spectra of the conjugate acids and of the anions of the phenolic compounds are also given. C.O.C.

Synthesis of Cyanine Dyes by Condensation of *p*-Dimethylaminobenzaldehyde with Appropriate Heterocyclic Compounds. IX— Four New Styrylcyanines

M. Q. Doja and A. K. Sinha

J. Indian Chem. Soc., **37** (March 1960) 146–150

Three styrylcyanine dyes have been prepared by condensing *p*-dimethylaminobenzaldehyde with 6-formamido-, 6-acetamido-, and 5-acetamidoquinaldine ethiodide and a fourth by condensing *p*-diethylaminobenzaldehyde with

5-acetamidoquinaldine ethiodide. Their absorption maxima, chemical, and physical properties including hues on silk, wool, and cotton and their fluorescence in weak alcoholic solution are given in tables. C.O.C.

Thiazolocarbocyanins with Aryl Radicals in Thiazole Nucleus. VII— Influence of Polar Groups in Thiazolocarbocyanins on their Colour

E. D. Sȳch

Ukrain. khim. zhur., **25** (No. 6) (1959) 767–773

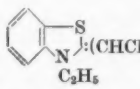
Several new thiazole derivatives were prepared. From the quaternary salts of these derivatives carbocyanine dyes were made. The nitro group in 5,5′-dinitrodiphenylthiazolocarbocyanine has a very strong bathochromic effect, considerably surpassing that caused by the strongest auxochromes such as phenolic groups in alkaline soln. and dialkylamines. T.Z.W.

Electronic Structure of Merocyanines

J. Nys *Compt. rend. congr. intern. chim. ind., 31e, Liège*, 1958 (Pub. as *Ind. chim. belge*, Suppl.), **2**, 505–511 (Pub. 1959)

Chem. Abs., **54** (25 March 1960) 5240

The C:O frequency determined in CCl_4, chlorobenzene, CH_3CN, and KBr is greater than usual; this shows that polarisation of the C:O group is abnormally weak for the ketomethylenic heterocycles $\overline{Y{\cdot}C(:X){\cdot}NZ{\cdot}C(:O){\cdot}CH_2}$ (Y, X, and Z = respectively, S, S, C_2H_5 (I); O, S, C_2H_5 (II); NC_2H_5, S, C_2H_5; CH_2, S, C_2H_5; CH_2, H_2, C_2H_5; S, C_6H_5N, C_2H_5; S, BrC_6H_4N, C_2H_5; S, $(C_6H_5)H$, C_4H_9; and for merocyanines in which R:$(CHCH)_n$; (R = 2-benzothiazolinylidene)—



is substituted at 5 in I (n = 0, 1, 2), II (n = 0) and $\overline{NC_6H_5{\cdot}C(:S){\cdot}NC_2H_5{\cdot}C(:O)}CH_2$; and quinoline and C_6H_5N at 5 in I. The decrease in polarisation depends on the structure of the ketomethylenic ring, but does not exclude presence of deep colour in solution or of appreciable dipole moment. This indicates that in some merocyanines the π-electrons are redistributed so that the "acidity" of the ketomethylenic ring is not solely caused (as usually accepted) by the O of the C:O group, but probably principally by a carbanion stabilised by induction. C.O.C.

Electronic Structure of Trinuclear Cyanines

A. van Dormael and J. Nys

Compt. rend. congr. intern. chim. ind., 31e, Liège, 1958 (Pub. as *Ind. chim. belge*, Suppl.), **2**, 512–517 (Pub. 1959)

Chem. Abs., **54** (25 March 1960) 5240

Absorption spectra 350–360 μ. and numerical values for λ_{max} and intensity are given for alcohol, 65% alcohol–35% lutidine, 35% alcohol–65% lutidine, and lutidine solutions of trinuclear cyanines. These spectra are compared with those of the corresponding trimethincyanines and dimethin merocyanines in alcohol and show three types of behaviour with change of solvent polarity. One type containing benzothiazole and indandione groups shows tautomeric equilibrium between the merocyanine and cyanine systems, evidenced by isobestic points. The second type of absorption compounds containing rhodanine and thiohydantoin groups, are similar to those of corresponding merocyanines; the spectra are not modified by the polarity of the solvent. The curves of the three types, containing pyrazolone or isoxazolone groups, show no isobestic points, but a cyanine system in polar solvents and an interface between merocyanine and cyanine systems in little polarised solvents. Possible configurations are given. C.O.C.

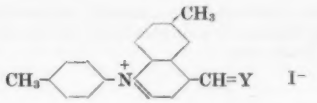
Synthetic Dyes

XV— Synthesis of *N*-*p*-Tolyl-6-Methyllepidinium Iodide and Its Transformations

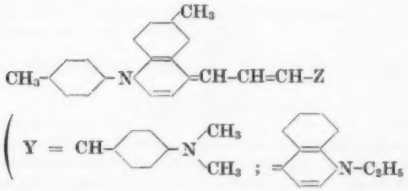
G. T. Pilyugin and B. M. Gutsulyak

Zhur. obshch. khim., **30** (April 1960) 1299–1302

The reaction of *pp*′-ditolylamine with acetone and paraformaldehyde in presence of HCl in dioxan yields 1-*p*-tolyl-6-methyllepidinium iodide which is used in the preparation of 5 new asymmetric cyanine dyes (A) of formula—



and



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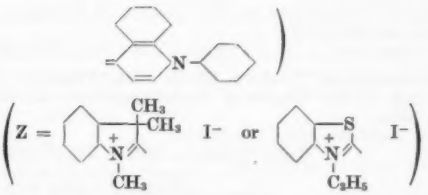


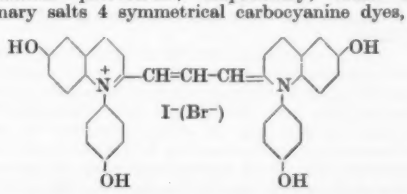
Absorption max. of A are compared with those of dyes prepared from *N*-phenyllepidinium iodide and it is shown that introducing methyl in 6-position to the phenyl group of the radical causes a slight bathochromic shift (4–6 mμ.); comparison with analogous isomers obtained from the quinaldinium salt shows a strong bathochromic displacement (50–58 mμ.) of the absorption max. Absorption curves (460–680 mμ.) of A are given.

XVI— Synthesis of Hydroxy- and Alkoxy-substituted Quaternary *N*-Arylquinaldinium Salts and their Transformations

G. T. Pilyugin and E. P. Opanasenko

Ibid., 1303–1307

The reaction of *p*,*p*′-dihydroxydiphenylamine, *p*-methoxyphenyl-α-naphthylamine, and *o*-methoxyphenyl-β-naphthylamine with paraldehyde and vinyl n-butyl ether (in acid soln.) yields 1-*p*-hydroxyphenyl-6-hydroxyquinaldinium iodide (bromide); 1-α-naphthyl-6-methoxyquinaldmium iodide, and 1-*o*-methoxyphenyl-5,6-benzoquinaldinium perchlorate, respectively; from these quaternary salts 4 symmetrical carbocyanine dyes, e.g.



have been prepared and their absorption max. in ethanol measured. In the above dye introduction of OH has caused strong bathochromic displacement (24 mμ.) compared with the analogous unsubstituted carbocyanine. G.J.K.

Mechanism of Dye Formation in Colour Photography. VII— Intermediate Bases in the Deamination of Quinonediimines

L. K. J. Tong, M. C. Glesmann, and R. L. Bent

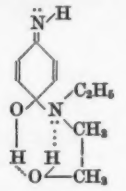
J. Amer. Chem. Soc., **82** (20 April 1960) 1988–1996

Deamination of certain oxidised derivs. of *p*-phenylenediamines in aq. soln. proceeds through stable intermediates which have been postulated as addition products with OH^-. Reaction rates measured by yields of indoaniline and indophenol dyes formed by coupling quinonediimines (QDI) or quinonemonoimines (QMI) respectively with α-naphthol. Deaminations of certain quinonediimines containing *N*-disubstituted group are $\propto$ $[OH^-]$ over pH range 8·0 to 12·0. Mechanism postulated is—

$$QDI^+ + OH^- \rightleftharpoons (QDIOH) \rightarrow QMI + \text{amine} \quad (1)$$

Equilibrium constants for (1) have been measured spectrophotometrically. Stability of intermediate (QDIOH) is

increased in case of diimines containing *N*-hydroxyalkyl group due to formation of a double ring system through intramolecular H-bonding—



Stability depends on whether positions of the two –OH groups permit formation of 5- or 6-membered rings. Ring system more probable if two β-hydroxyethyl groups present. F.J.

Effect of Structure on the Change in Colour of Vat Dyes on Soaping
J. Wegmann J.S.D.C., **76** (May 1960) 282–300

Formation of Carbon Black (C.I. Pigment Black 6 and 7) by Thermal Decomposition of Hydrocarbons
I. S. Rafal'kes and P. A. Tesner
Trudy Vsesoyuz. Nauch.-Issledovatel. Inst. Prirod. Gazov (3) (1958) 3–33
Chem. Abs., **54** (25 March 1960) 6089

Thermal decomposition of CH_4, natural gas containing 90% CH_4, and benzene was studied at a flow of 500 ml./min. at 1150–1450°C. The velocity of growth of the Carbon Black deposit, at residence time τ of the gas, was $v = kr_{max}/\tau$ (r_{max} = maximum radius of the pigment particles obtained). The yield of pigment in the decomposition of natural gas was 18·5% at 1150°C., 43·7% at 1300°C., and then remained at 45·8% up to 1450°C. The H formed slowed down the deposition of pigment on the reactor walls. This effect occurred with all gases which decomposed with increase in volume. Although the activation energy of the Carbon Black nuclei formation from the three sources was approx. 1000 kcal./mol., increase in temperature did not increase the dispersity of the pigment, because it is formed earlier than when the gas reached maximum temperature. The effect of the H formed on the dispersity of the pigment was investigated in detail. C.O.C.

Fluorescence Properties of Intermediates in Photoreduction of Chlorophyll-a (C.I. Natural Green 3) and Evidence for Complex Formation in Solution
S. S. Brody
J. Amer. Chem. Soc., **82** (5 April 1960) 1570–1574

Two intermediate forms of chlorophyll produced during photoreduction of Chlorophyll-a in presence of phenylhydrazine have been established. One form has fluorescence max. at 625 mμ., the action spectrum for exciting this fluorescence having maxima at 420, 570, and 615 mμ. The second form has a fluorescence max. at 545 mμ. the maxima of the action spectrum being 410, 500, and 520 mμ. From this evidence and fluorescence and action spectra at −193°C. complex formation between chlorophyll and phenylhydrazine is indicated for this photoreduction. F.J.

Aluminium and Aluminium-based Paints and Their Analysis
A. Zambrini
Pitture e vernici, **35** (1959) 321–327, 407–446, 875–879
Chem. Abs., **54** (10 April 1960) 7177

Differentiates between the several aluminium pigments (C.I. Metal Pigment 1) at present being commercially produced, details their characteristics and properties and gives a brief account of the methods used in their production. Qualitative and quantitative methods of analysis of aluminium pigments are critically discussed. C.O.C.

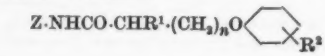
Titanium Spinel Pigments
K. Takahashi and A. Otsuka
Yogo Kyokai Shi, **67** (1959) 139–141

When Mg and Zn in $2MgO.TiO_2$ and $2ZnO.TiO_2$ are replaced by Co and Ni, pigments of various hues are produced. The CoO–MgO–TiO_2 system showed a wide variety of hues from light blue to dark green. The NiO–ZnO–TiO_2 system yielded light greens. The system NiO–CoO–MgO–TiO_2 gave yellowish to brilliant greens and CoO–ZnO–TiO_2 gave light to dark yellowish browns. C.O.C.

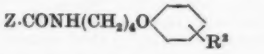
PATENTS

Colour Couplers containing Mono-n-alkyl Groups
Eastman Kodak Co. *USP* 2,908,573 (25 July 1956)

Compounds of formula—



or



(Z = phenolic hydroxyl, pyrazolone or benzoyl acetamide group capable of coupling with the oxidation product of a primary aromatic developer and contains at least 1 Ar; R^1 = H or C_2H_5; R^2 = n-Alk of 7–15 C), e.g. α-(3-n-pentadecylphenoxy)acetic acid, are colour couplers of exceptionally low m.p. and so of less tendency to crystallise in the emulsion. C.O.C.

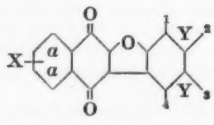
ω-Aldehydes of *N*-Substituted ω-Cyanomethylene Indoline Derivatives—Dye Intermediates
FBy *BP* 833,859 (Germany 5 June 1957)

Compounds of formula—

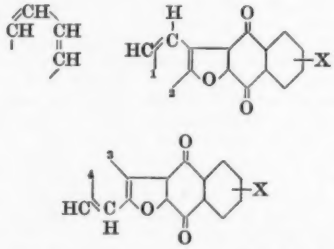
(A = phenylene substituted in 5- and 6-positions by H, Cl, Br, OCH_3, OC_2H_5, SC_2H_5, SCH_2, C_6H_5, NO_2 or NR^1R^2 (R^1 and R^2 = H, CH_3, C_2H_5, C_3H_7, C_4H_9, CH_2CH_2OH, CH_2CH_2Cl, and CH_2CH_2CN) or naphthylene; X = C dialkylated with CH_3, C_2H_5, C_3H_7 or C_4H_9; Y = N monosubstituted by satd. Alk of < 19 C or phenyl; Z = H or CN; *n* = 0 or 1) are useful intermediates for dyes. Thus condensed with aromatic amines they yield azomethin dyes. C.O.C.

Heterocyclic Vat Dye Intermediates
General Aniline *BP* 835,908 (U.S.A. 30 Dec 1955)

The title compounds are multi-component mixtures of compounds—



(X = NO_2 or NH_2 in α-position; one adjacent pair of Y valencies are bonded to H atoms, the other pair to a group of formula—

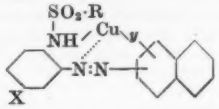


They are obtained by reacting 8-nitro-2,3-dichloro-1,4-naphthoquinone with 1-hydroxy-, 2-hydroxy-, 1,5-dihydroxy- or 2,6-dihydroxynaphthalene at elevated temperatures in presence of an organic tertiary base, especially pyridine, as acid-bonding agent, and (optionally), reducing the $-NO_2$ groups. They are vat dye intermediates, e.g. where X = NH_2, by acylation with, e.g. benzoyl or terephthaloyl chloride, or condensation with halogenoanthraquinones, followed by carbazole ring closure. A.T.P.

Metal-complex Monoazo Dyes for Wool, etc.
S *BP* 835,772 (Switzerland 18 Nov 1955)

Monoazo compounds *o*-halogenoaniline → *o*-coupling naphthol or naphthylamine, containing at least one water-solubilising group, e.g. COOH, SO_3H, $SO_2{\cdot}NH_2$, or

SO_2·Alk, are heated with a Cu compound and an organic sulphonamide to give complexes—

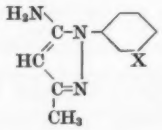


(X = a substituent; R = Alk or Ar; y = O, NH, or NR), which may be used as wool dyes, or demetallised and then made into Co- or Cr-complex dyes. Thus the monoazo compound 2-chloroaniline-5-sulphonamide → 1-acetylamino-7-naphthol suspended in aq. NaOH is boiled with *p*-toluenesulphonamide, whilst adding slowly an aq. soln. of $CuSO_4$ containing glycerine. Cu is removed from the complex by boiling with aq. Na_2S, and the Cr-complex can then be formed by heating in formamide with chromium formate; it dyes wool and nylon grey from an acid bath. E.S.

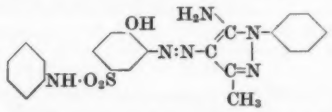
Metal(Chromium and Cobalt)-complex Monoazo Dyes for Wool, etc.

S *BP* 837,716 (15 March 1957)

Sulphonamides of *o*-aminophenol, *o*-anisidine or anthranilic acid are diazotised and coupled with 5-aminopyrazoles—



(X = H or Cl) and the products converted into their 1:2 Co or Cr complexes, which dye wool, nylon, etc., orange, brown or brown-red from neutral or weakly acid baths. Thus 2-aminophenol-4-sulphonanilide is diazotised and coupled with 5-amino-3-methyl-1-phenyl pyrazole to give—

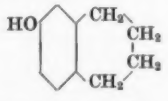


which is stirred with $CoSO_4$ in formamide at 94–97°C. The Co-complex so formed dyes wool yellowish-brown. E.S.

Brown Metal-complex Monoazo Dyes for Wool and Nylon

General Aniline *BP* 836,995 (U.S.A. 28 June 1955)

The title dyes are obtained by coupling diazotised 2-amino-4-nitrophenol (I), which may be substituted in the 6-position by Hal or a sulphamyl or subst. sulphamyl group, with 2-tetralol (II)—

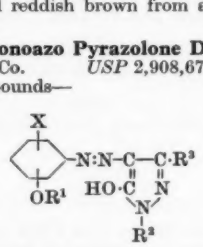


and converting into the 1:2 metal-complexes, preferably with Co or Cr compounds. The coupling component is prepared from tetrahydronaphthalene by sulphonation followed by fusion with KOH. Thus the Co-complex of the monoazo dye I → II, dried in presence of a dispersing agent, dyes wool reddish brown from a bath containing $(NH_4)_2SO_4$. E.S.

Metallisable Monoazo Pyrazolone Disperse Dyes

Eastman Kodak Co. *USP* 2,908,677 (30 March 1955)

Monoazo compounds—



(R^1 = CH_3, C_2H_5 or C_2H_4OH; X = H, OCH_3, OC_2H_5 or OC_2H_4OH; R^2 = H, phenyl, methylphenyl, chlorophenyl, etc.; R^3 = CH_3, COOH, COOAlk, NH_2, OH or CF_3; OR^1 is *o*- or *p*- to the azo link) may be metallised on cellulose acetate, especially with $Ni(SCN)_2$ to give dyeings of good wet fastness. Thus diazotised 2,5-dimethoxyaniline is coupled with 3-methyl-1-phenyl-5-pyrazolone. The product dyes cellulose acetate and nylon bright yellow without staining any cellulose present. Padding the dyeing on cellulose acetate with aq. $Ni(SCN)_2$ and steaming increases the fastness to light and washing. E.S.

Yellow Chromium-complex Monoazo Pyrazolone Dyes

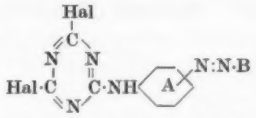
S *BP* 834,270 (Switzerland 12 Oct 1955)

Chromium-complex dyes for wool, or for colouring solvents, similar to those of *BP* 753,550 (J.S.D.C., **72** (1956) 544) are made by diazotising anthranilic acid (I), which may carry in the 4- or 5-position a sulphamyl or subst. sulphamyl group, coupling with a 1-(5′,6′,7′,8′-tetrahydro - 1′)naphthyl - 3 - methyl - 5 - pyrazolone - 4′ - sulphonamide (II) in which the amide N may carry substituents such as Alk, Ar, etc., and converting into the 1:2 metal-complex. Thus I is diazotised and coupled with II, and the product heated in ethylpolyglycol with chromium formate to give the complex which dyes wool and nylon greenish yellow. E.S.

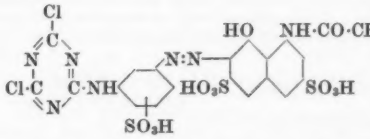
Monoazo Reactive Dyes for Cellulose

ICI *BP* 837,035 (5 June 1957)

The title dyes of formula—



(the nucleus A may be further subst. other than by OH or amino; B = *o*-coupling naphtholsulphonic acid, which may contain amino, etc., groups) are prepared by condensing 1 mol. of e.g. cyanuric chloride (I) with a suitable phenylenediamine, followed by diazotisation and coupling with a naphtholsulphonic acid. Or a diazotised nitro- or acylamino-aniline is diazotised and coupled with a naphtholsulphonic acid, the nitro group is reduced or the acylamino group hydrolysed, to give an amino-monoazo compound, which is condensed with I. Thus the condensation product of 1,3-phenylenediamine-4-sulphonic acid with I mol. of I is diazotised and coupled with *N*-acetyl-H acid to give—

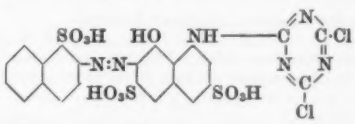


which is salted out and dried in presence of suitable buffer salts. It dyes cellulose bluish red by processes which include aftertreatment with acid-binding agents. E.S.

Red and Violet Monoazo Reactive Dyes for Cellulose

ICI *BP* 836,248 (26 June 1957)

The title dyes are prepared by condensing 1 mol. of a cyanuric trihalide with a monoazo compound naphthylaminesulphonic acid → 1-amino-8-naphthol-6-sulphonic acid (or 3,6- or 4,6-disulphonic acid) (alkali-coupled). Or the cyanuric trihalide may be condensed with 1 mol. of the coupling component before coupling. Use of 2-naphthylamine-1-sulphonic acid (I) as diazo component leads to dyes of good fastness to bleaching. Thus an aq. solution of the monoazo compound I → H acid (alkali-coupled) is added at < 3°C. to an aq. suspension of cyanuric trichloride, giving—

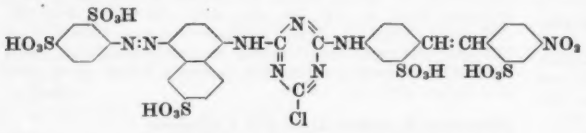


which dyes cotton bluish-red. E.S.

Yellow and Orange Monoazo Reactive Dyes for Cellulose

ICI *BP* 837,953 (23 Aug 1957)

Suitable 2,4-dihalogeno-6-amino-s-triazines are condensed with 1 mol. of a 4-benzoazo-1-naphthylamine, to give the title dyes, which contain at least two water-solubilising ($COOH$ or SO_3H) groups. Or cyanuric chloride (I) may be condensed first with 1 mol. of the aminoazo compound and then with 1 mol. of NH_3 or a suitable amine, which must be incapable of coupling with diazo compounds. They are more stable in aq. solutions of acid-binding agents than the similar dyes of *BP* 797,946 (J.S.D.C., **74** (1958) 714) obtained by condensing 1 mol. of I with 1 mol. of an aminoazo compound, and which consequently contain 2 reactive Cl atoms. Thus I is condensed with the aminoazo compound aniline-2,4-disulphonic acid → 1-naphthylamine-6-sulphonic acid, and the product is then further condensed with 4-amino-4′-nitrostilbene-2,2′-disulphonic acid to give—

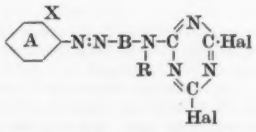


which dyes cellulose bright yellow from a hot alkaline dyebath. E.S.

Copper-complex Monoazo Reactive Dyes for Cellulose

ICI *BP* 837,124 (5 July 1957)

The title dyes are 1:1 complexes of monoazo compounds—

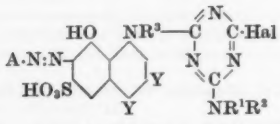


(the ring A is free from SO_3H but contains other substituents, especially sulphamyl; X = substituent capable of metal-complex formation; B = residue of an *o*-coupling naphtholsulphonic acid; R = H or Alk) and give orange, red, and reddish-blue when applied to cellulose with an alkaline aftertreatment. Thus diazotised 2-aminophenol-4-sulphonamide is alkali-coupled with J acid, and the product is boiled with aq. $CuSO_4$ to give the Cu-complex. Condensation with a suspension of cyanuric chloride in presence of aq. Na_2CO_3 gives a rubine reactive dye. E.S.

Red Monoazo Reactive Dyes for Cellulose

ICI *BP* 834,304 (23 April 1957)

Monoazo compounds—



(A = Ar of benzene series free from OH or amino groups; R^1 = H, Alk, Ar; R^2 = H, Alk or hydroxyalkyl, or NR^1R^2 = piperidyl or morpholyl radical; A and R^1 are different, but one or both contain at least one SO_3H group; R^3 = H or Alk; one Y = SO_3H, the other Y = H) combine with cellulose under alkaline conditions to give fast reds. Thus cyanuric trichloride is condensed first with 1 mol. of NH_3 and then with 1 mol. of H acid. Coupling with diazotised orthanilic acid then gives the red reactive dye (A = *o*-$C_6H_4{\cdot}SO_3H$; R^1, R^2, R^3 = H; Hal = Cl; the *α*-Y = H, the *β*-Y = SO_3H). E.S.

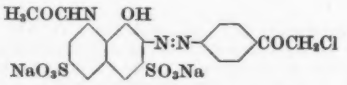
Reactive Dyes for Cellulosic Fibres

BASF *BP* 831,371 (Germany 23 March 1957)

Cellulosic fibres are coloured highly fast to washing and rubbing by dyes which contain at least one group—

$$-CO-Y-C(R^1)(R^2)X$$

(Y = direct link, alkylene or phenylene, which may be subst., R^1 and R^2 = H, Alk, aralkyl, cycloalkyl or phenyl, X = Hal) by treating before, during, or after application of the dye with an alkaline agent, and finally heating for a short time at 90–160°C. The dyes may be of various chemical classes, e.g. acid and substantive azo and azomethin dyes and acid anthraquinone dyes. Thus, cotton fabric is padded at 25°C. with an aq. soln. containing, per litre, the dye (15)—

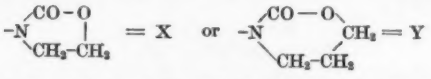


obtained by coupling diazotised 4-amino-*ω*-chloracetophenone with 8-hydroxy-1-acetamidonaphthalene-3,6-disulphonic acid), $NaHCO_3$ (10) and NaCl (50). It is squeezed to 100% moisture content, dried, heated for 3 min. with air at 100°C., and soaped to give a pink of good fastness to light, washing, and rubbing. A.T.P.

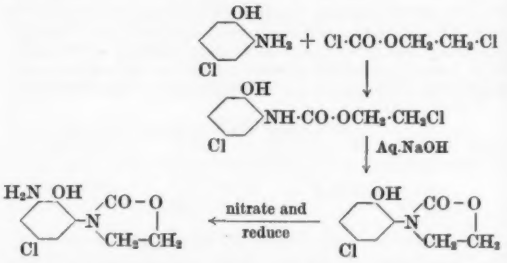
Metal(Chromium and Cobalt)-complex Heterocyclic Monoazo Dyes for Wool, etc.

S *BP* 835,470 (Switzerland 20 July 1956)

Monoazo compounds having chelatable groups in the *oo′*-positions and also 1 or 2 substituents—



give 1 : 2 metal-complexes with Cr and Co which dye wool, nylon, etc., from neutral or weakly acid baths. Thus 2-amino-4-chloro-6-X-phenol is prepared by the route

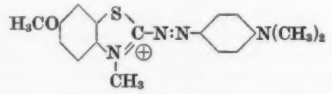


and is diazotised and coupled with *N*-acetyl-1-amino-7-naphthol. Boiling with aq. chrome alum gives the Cr-complex which dyes wool and nylon blue-grey. E.S.

Basic Monoazo Dyes for Cellulose Acetate

BASF *BP* 837,472 (14 June 1955)

Suitable *N*-cyclic primary amines are diazotised and coupled with aromatic (preferably tertiary) amines, and the products made into quaternary compounds by alkylation or aralkylation to give bright red, violet, and blue basic dyes of high fastness to burnt gas fumes on cellulose acetate. Instead of diazo coupling, the *N*-cyclic amine may be condensed with a nitroso compound of the aromatic amine. An example is the bright blue—

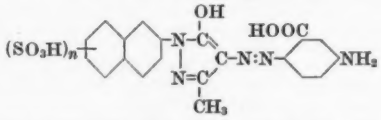


E.S.

Metallisable Yellow and Orange Pyrazolone Disazo Direct Dyes

S *BP* 835,490 (Switzerland 21 Dec 1956)

Two mol. of aminomonoazo compounds—

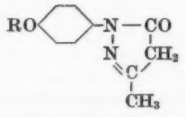


(*n* = 1 or 2) are condensed with 1 mol. of a dibasic carboxylic acid dichloride containing at least one C:C group to give the title dyes. Metal-complex formation may be accomplished in substance or on the fibre, or if *n* = 2

complexing precedes condensation with the acid chloride. Cu and Ni are the preferred metals, and the products reserve wool and nylon well, and cellulose acetate, polyester, and polyacrylonitrile fibres very well. Thus 5-nitroanthranilic acid is diazotised and coupled with 3 - methyl - 1 - naphthyl(2′) - 5 - pyrazolone - 5′,7′ - disulphonic acid, and the nitro group is then reduced to give an NH_2 group. Heating to 70–80°C. in aq. ammoniacal $CuSO_4$ gives the Cu-complex of the aminomonoazo compound which is condensed in chlorobenzene with fumaryl dichloride to give the yellowish orange direct dye. E.S.

Orange and Red Pyrazolone Disazo Pigments
ICI *BP* 835,618 (31 July 1957)

Pyrazolones—



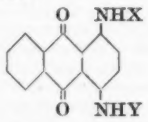
(R = Alk of < 4 C) are coupled with tetrazotised benzidines carrying Cl, OCH_3, C_6H_5, or COOAlk in the 3,3′-positions to give the title products, which give browns when mixed with carbon black as described in *BP* 642,204 (J.S.D.C., **66** (1950) 654). Thus tetrazotised 3,3′-dichlorobenzidine is coupled with 2 mol. of 1-*p*-methoxyphenyl-3-methyl-5-pyrazolone dissolved in aq. NaOH. The product gives deep reds when incorporated in rubber, polyvinyl chloride, cellulose acetate or polyethylene. E.S.

Solvent Dyeing of Azoic Dyes on Polyester Fibres
FH *BP* 835,441 (Germany 4 Nov 1955)

Suitable combinations of diazotisable amines and coupling components can be applied to Terylene from solvent solution, followed by steaming or dry heat treatment, diazotisation and coupling being then effected by treatment in hot aq. nitrous acid. Thus piece goods are padded at 60°C. with a solution of the *o*-anisidide of 3,2-hydroxynaphthoic acid (5 g.) and 2-amino-5-nitroanisole (4 g.) in ethylene glycol or butanol (100 c.c.), squeezed, and steamed 10 min. at 98–103°C. A deep red is then produced by treating at 80°C. in a solution containing per litre of water, 3 g. $NaNO_2$ and 4 c.c. H_2SO_4 96%. E.S.

Bromoalkylaminoanthraquinones— Blue Disperse Dyes for Nylon
ICI *BP* 836,671 (24 Jan 1958)

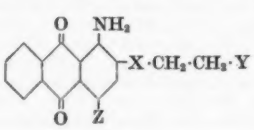
The title compounds—



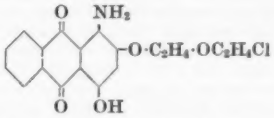
(X, Y = same or different mono- or dibromoalkyl) are obtained, e.g. by treating mono- or dihydroxyalkylaminoanthraquinones with thionyl bromide or PBr_3, or, where one of X, Y is dibromoalkyl, by bromination of a monobromoalkyl or alkenyl derivative. Thus, 1,4-bis-(hydroxy-iso-propylamino)anthraquinone (7·1) is heated at 40°C. in ethylene dibromide (46) and pyridine (5). Thionyl bromide (12·5) is added, and after being stirred for 6 hr. at 40°C., the product is filtered at 20°C., washed with ethylene dibromide (8) and water and dried at 80°C. It dyes nylon bright reddish-blue of excellent wash fastness. The dyes may also be used on sec. acetate, triacetate, and Terylene, but it is preferable to treat the fibre before, during or after dyeing with an amine, phenol or thiophenol to obtain blues of excellent washing and light fastness. A.T.P.

Anthraquinone Disperse Dyes
ICI *BP* 835,819 (14 Oct 1957)

Red to bluish-red disperse dyes of high affinity and excellent fastness to light, gas-fumes, and sublimation are—



(X = O or S, Z = OH or NH_2, Y = Cl, Br, aryl, aryloxy, arylthio, arylsulphonyl, $-OCH_2CH_2R$, $-S{\cdot}CH_2CH_2R$, or $-SO_2{\cdot}CH_2CH_2R$, and R = Cl, Br, OH, aryloxy, arylthio, arylsulphonyl, β-hydroxyethyl, β-chloroethoxy, β-bromoethoxy, β-arylamino or β-*N*-aryl-*N*-alkylamino. When X = S, Y is not halogen). Especially useful are dyes where Y contains a β-chloro- or β-bromoethyl group. They are obtained by any of the conventional methods, e.g. condensation of 1-amino-2-bromo-4-hydroxyanthraquinone or 1-amino-2-phenoxy-4-hydroxyanthraquinone (I) with hydroxy compounds (X = O) or through 1-amino-2-mercapto-4-hydroxyanthraquinone (X = S). Thus, diethylene glycol (215) and KOH (6) are heated for 1 hr. at 170–175°C. to remove H_2O. I (26) is added at 100°C. and the mixture stirred for 18 hr. at 120–125°C., cooled to 20°C. and 1-amino-4-hydroxy-2-β-(β-hydroxyethoxy)-ethoxyanthraquinone (II), a bright red dye of excellent fastness, isolated by addition of H_2O (150) and $NaHCO_3$ (9). II (14·8), monochlorbenzene (27·5), pyridine (5) may then be stirred at 65–70°C. and thionyl chloride (6·5) added over 30 min. before stirring for 1 hr. at 70°C. Chlorobenzene is removed by steam distillation and the product—



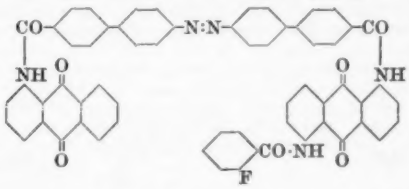
filtered. It colours synthetic fibres bright red of excellent fastness to light and sublimation. A.T.P.

Disulphonated 1,4 - di - (*p* - cyclohexylphenylamino-anthraquinones— Acid Dyes
By *BP* 837,935 (Germany 5 July 1957)

The free acids of the title compounds are more soluble in water than their alkali metal or NH_4 salts. Sulphonation of the anthraquinone compound (I) can be carried out in fuming sulphuric acid and the product obtained in almost quantitative yield by dilution to 16–20% H_2SO_4 with water and filtration. Electrolytes containing metallic or ammonium salts and anions of acids must be absent throughout. Thus I (1) is sulphonated at 10°C. in 12% oleum (10) and the dye isolated by dilution with H_2O (45) to 18% H_2SO_4, filtration and washing with 9% HCl. Its solubility in water is 60–80 g./l. compared with 10 g./l. for the Na salt. A.T.P.

Yellow Azo Anthraquinone Vat Dye
Ciba *BP* 834,456 (Switzerland 20 Jan 1956)

4,4′-Azodiphenyl-4″,4‴-dicarboxylic acid dichloride (I) is condensed with a mol. of 1-aminoanthraquinone (which may carry Hal in the 6- and/or 7-positions) and with 1 mol. of a 1-amino-5-benzoylaminoanthraquinone, preferably containing F in the 2′-position of the benzoyl group, to give the title dyes. Thus I is stirred in trichlorbenzene containing pyridine with 1-aminoanthraquinone at 85–95°C. 1-Amino-5-*o*-fluorobenzoylaminoanthraquinone is then added, and the mixture is boiled giving—



which dyes greenish yellows fast to light and chlorine from a bordeaux vat. E.S.

Dibenzpyrenequinone Vat Dyes
FH *BP* 837,298 (Germany 1 Sept 1955)

Fast to light brown vat dyes are obtained by cyclising a reaction product of a dihalogeno-3,4,8,9-dibenzopyrene-5,10-quinone and an aminoanthraquinone-arylacridone with an $AlCl_3$/NaCl mixture in absence or presence of urea, a molecular compound of $AlCl_3$ and SO_2, conc. H_2SO_4 or monohydrate at 90–150°C. Thus, a dull brown dye of excellent light fastness is from dibromo-3,4,8,9-dibenzopyrene-5,10-quinone and 4-aminoanthraquinone-2,1-benzacridone (*GP* 545,000), followed by cyclisation. The

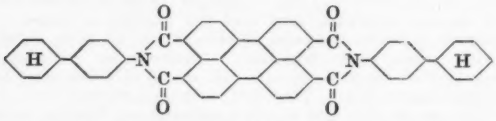
dyes are related to the brown vat dyes of *BP* 332,579 and *BP* 519,123 (J.S.D.C., **56** (1940) 368), but these have poor light fastness. A.T.P.

Linear Polyanthrimidecarbazoles— Grey Vat Dyes
Ciba *BP* 835,714 (Switzerland 3 April 1956)

Condensation of a 1,4-diaminoanthraquinone (I) with a 1,4-dichloroanthraquinone (II), optionally in presence of an α-monochloroanthraquinone (III), followed by treatment of the resulting linear polyanthrimide with a carbolising agent in presence of a tertiary base free from –OH groups gives grey pigments and vat dyes of excellent fastness to chlorine and light and which yield the same hue whether dyed at high or moderate temperatures. Advantageously, at least 0·2 mol. II per mol. of I is used and the molar ratio of all components is such that the ratio of exchangeable Cl atoms to $-NH_2$ groups is $> 0{\cdot}6 : 1$, preferably $0{\cdot}8 : 1$ to $1{\cdot}5 : 1$. When the ratio of II : I does not permit this, III may be added as necessary, preferably substantially after completion of the reaction between I and II. Thus, 1,4-diaminoanthraquinone (6), 1,4-dichloroanthraquinone (3·5), Na_2CO_3 (6·9), Cu_2Cl_2 (0·2), Cu acetate (0·2) and nitrobenzene (110) are stirred at 200–205°C. for 6 hr. 1-Chloro-4-benzoylaminoanthraquinone (9) is added and the mixture refluxed for 9 hr., cooled to 50°C. and filtered. The cake is washed with nitrobenzene and alcohol and extracted with boiling 5% HCl, filtered, and washed. Carbolisation of this linear polyanthrimide with $AlCl_3$ in anhydrous pyridine at 140°C. yields a fast grey vat dye. A.T.P.

Perylene Tetracarboxylic Acid Class Dyes
FH *BP* 837,326 (Germany 14 March 1956)

Perylene-3,4,9,10-tetracarboxylic dianhydride (I) is condensed with *p*-cyclohexylaniline in, e.g. quinaline at 220–230°C. or dil. HCl at 210–220°C. under pressure to give the red dye—



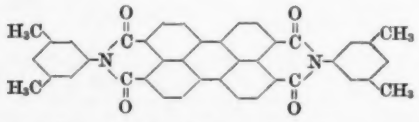
It is used in lacquers, printing inks, and plastics, e.g. poly(vinyl chloride) compositions or polyethylene, and has excellent clarity and fastness to oil, overspraying, solvents, bleeding, and light. These properties are not found in similar dyes described in *BP* 201,786 and *BP* 659,529 (J.S.D.C., **68** (1952) 131).

BP 837,327 (Germany 22 June 1956)

A red dye of similar properties to the above is that from (I) and *m*-toluidine. A.T.P.

Red Pigment of the Perylene Tetracarboxylic Acid Series
FH *BP* 835,459 (Switzerland 22 March 1956)

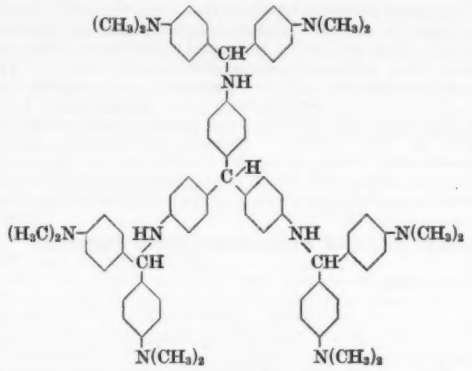
Condensation of perylene-3,4,9,10-tetracarboxylic acid or anhydride with 3,5-dimethylaniline yields a red pigment suitable for printing inks, lacquers, plastics, and spinning dopes—



It has excellent clarity and fastness to oil, over-spraying, solvents, bleeding, and light. Previously known analogues from 2,4- and 2,6-dimethylaniline had only poor fastness properties. A.T.P.

Leucauramine Derivatives
Caribonum *BP* 835,809 (21 Aug 1957)

Colourless leucauramine derivatives which when subject to e.g. slightly acidic oxidising conditions, are converted to fast to light blue and violet compounds, are obtained by condensing a tri-(*p*-aminophenyl)methane, in which phenyl may be subst. by Alk, with Michler's hydrol (I). They are used on transfer sheet materials, typewriter ribbons, etc. Thus—



from (I) and tri-(*p*-aminophenyl)methane. A.T.P.

Acylated Leuco Methylene Blue
General Aniline *USP* 2,909,520 (6 Dec 1957)

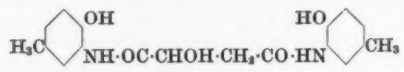
Methylene Blue (C.I. 52015) is reduced in presence of a water-immiscible organic liquid which is a solvent for the desired acylated product. It is then acylated at pH 3–6 and the product isolated by conventional methods. Thus Methylene Blue chloride (32 g.), chlorobenzene (250 ml.), distilled water (300 ml.), and ethylenediaminetetraacetic acid (5 g.) are placed in a flask and 15 N-NaOH (13·3 ml). added while stirring. This is followed by 36 g. Na hydrosulphite (C.I. Reducing Agent 1). After 5 min. benzoyl chloride (35 ml.) is added. The pH is allowed to drop to 4 and kept at that figure by adding NaOH as necessary. The mixture is stirred at this pH for 2 hr. Activated charcoal (5 g.) and Attapulgus clay (7 g.) are then added and then NaOH to bring to pH 10. The organic layer is then separated off and distilled to dryness. This gives a 93% yield of the colourless benzoyl leuco Methylene Blue. C.O.C.

Acylamino Derivatives— Intermediates for Diaryloxazoles
Ciba *BP* 835,893 (Switzerland 17 June 1955)

Acylamino compounds—

$$HOR^1{\cdot}NH{\cdot}CO{\cdot}R^3{\cdot}CO{\cdot}NH{\cdot}R^2{\cdot}OH$$

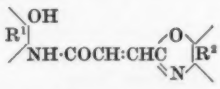
(R^1 and R^2 = same or different Ar where –OH is *ortho* to –NH and Alk, alkoxy, Hal or nitro may also be present, R^3 = $-CH(OH)CH_2-$ or $-CH(OH)CH(OH)-$) are obtained by condensation on both –COOH groups of tartaric or malic acid with an *o*-hydroxyaminobenzene. They are intermediates for dyes and fluorescent brightening agents. Thus, 1-amino-2-hydroxy-5-methylbenzene (369), malic acid (208), and chlorobenzene (2000) are stirred under gentle reflux for 8 hr. in absence of air, the water of reaction being continually removed. On cooling, filtering, and washing with alcohol and benzene, the acylamino-derivative—



is obtained. A.T.P.

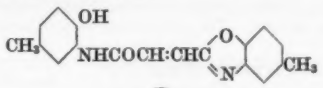
Aryloxazolyl-Ethyiene Compounds
Ciba *BP* 835,896 (Switzerland 15 June 1956)

The title compounds—



(R^1 and R^2 are as in *BP* 835,893 above) are obtained by condensation of 2 mol. of an *o*-hydroxyaminoaryl compound with 1 mol. of thiomalic acid or its alkyl mono- or di-ester. They are intermediates for fluorescent brightening agents (see *BP* 835,897 below). Thus 1-amino-2-hydroxy-5-methylbenzene (66·5) and chlorobenzene (700) are stirred in absence of air. *dl*-Thiomalic acid (37·5) is added and the mixture heated in 30 min. to 130°C. and maintained at 130–135°C. for 12 hr., with removal of water of reaction and H_2S. Chlorobenzene is steam

distilled off and, on cooling, the product is filtered and recrystallised from benzene—



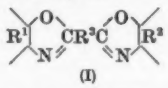
(I)

A.T.P.

α,β-Di-[Aryloxazolyl-(2)]-Ethylene Compounds—Fluorescent Brightening Agents

Ciba *BP* 835,892 (Switzerland 17 June 1955)

The title compounds, of general formula—



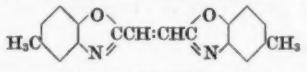
(I)

(R^1 and R^2 = Ar (I), same or different, and which may contain Alk, nitro or chloro, especially Alk where combined subst. in R^1 and R^2 have 2–4 C, and R^3 = organic bridge containing at least one double bond, e.g. vinylene) are obtained by elimination of H_2O, e.g. with $ZnCl_2$ at 160–180°c., from the acyl derivatives of *BP* 835,891, viz. those obtained by condensation of dihalides of unsaturated dicarboxylic acids, e.g. fumaric acid, with *o*-hydroxyarylamines. The title compounds are thus produced more readily and purer than by previously known methods involving reaction of hydroxy compounds with dicarboxylic acids of the succinic acid type and subsequent dehydrogenation, or by fusion of hydroxyaminoaryl compounds with unsaturated dicarboxylic acids. They can, in addition to known uses, be used as fluorescent brightening agents for lacquers and plastic masses. Thus, to a melt of ethylene glycol (10) and $ZnCl_2$ (150) is added over 15 min. at 155–160°c. the acylamino compound (30)—

The mixture is stirred at 160–165°c. for 10 hr. and then diluted slowly with cold water (600). After acidifying with HCl and stirring 1 hr. at 60°c. the product is filtered, washed with H_2O and (optional) crystallised from dioxan to give αβ-di-[5,7-dimethylbenzoxazolyl-(2)]-ethylene, whose solution in dioxane has a bluish fluorescence.

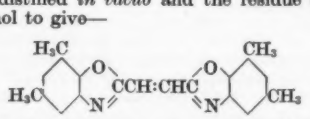
BP 835,894 (Switzerland 17 June 1955)

The acylamino derivatives of *BP* 835,893, when heated at 140–180° with agents which split off H_2O, e.g. $ZnCl_2$, H_3BO_3, glacial acetic acid, yield the title compounds of general formula (I) above [R^3 = –CH=CH– or –CH=C(OH)–]. They are fluorescent brightening agents. Thus, the acylamino derivative from 1-amino-2-hydroxy-5-methylbenzene and malic acid (see *BP* 835,893) on heating with $ZnCl_2$ and H_2O at 160–170°c. for 10–18 hr. gives αβ-di-[5-methylbenzoxazolyl-(2)]ethylene—



BP 835,895 (Switzerland 15 June 1956)

Fluorescent brightening agents are obtained by condensing at elevated temperatures approx. 2 mol. of an *o*-hydroxyaminoaryl compound with 1 mol. of fumaric, malic or aspartic acid or their alkyl mono- or di-esters, and without separating, cyclising with an agent capable of splitting off H_2O, or, if malic or aspartic acid is used, eliminating H_2O or NH_3 respectively. The products are thus obtained more readily and purer than by previous methods. Thus, 2,4-dimethyl-6-aminophenol (13·7), malic acid (6·7), and H_3BO_3 (0·2) are refluxed in xylene (100) for 6 hr. in absence of air, water being continually removed. Xylene is distilled *in vacuo* and the residue crystallised from ethanol to give—



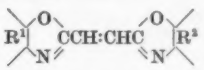
The products have formula (I) (R^3 = CH:CH).

BP 835,897 (Switzerland 15 June 1956)

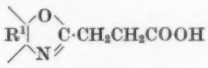
Elimination of water from the aryloxazolyl ethylene compounds of *BP* 835,896 gives similar compounds to those of *BP* 835,895. Thus I (see *BP* 835,896) (80–90) is added over 15–30 min. to a melt at 160–168°c. of H_2O (30) and $ZnCl_2$ (450). After stirring 6 hr., H_2O (450) is added dropwise and the mixture stirred at 90–100°c. until a solution is formed. The solution is cooled to 50–70°c. and added to H_2O (900) and HCl (60), stirred for 1 hr., filtered and the cake washed with warm water to give αβ-di-[5-methylbenzoxazolyl-(2)]ethylene.

BP 835,898 (Switzerland 17 June 1955)

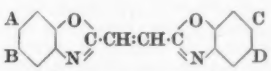
A general claim for—



(R^1 and R^2 = benzene residues and contain at least one CH_3 between them). They can be obtained by known methods, e.g. melting a methyl-*o*-hydroxyaminobenzene (I) with fumaric acid or condensing I with succinic acid and then dehydrogenating the αβ-di[benzoxazolyl-(2)] ethane (II). II can also be obtained by condensation of an *o*-hydroxyaminobenzene with succinic acid, and condensing the product with—



This latter route is especially useful where R^1 and R^2 are different. New methods, especially suitable for compounds where R^1=R^2 are by any of the methods outlined in *BP* 839,891 to 835,897 inclusive and special claim is made for—

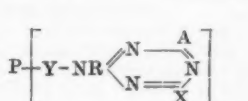


where (i) A=C=H, B=D=CH_3, (ii) A=C=CH_3; B=D=H, (iii) B=CH_3, A=C=D=H. They are very active fluorescent brightening agents suitable for a wide range of materials, e.g. for lacquers, films, and especially synthetic fibres, on which, when applied from an aq. dispersion, they have excellent light fastness (cf. previously known compounds where R^1 and R^2 are unsubstituted, which have poor light fastness). A.T.P.

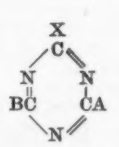
Phthalocyanine Reactive Dyes

ICI *BP* 836,647 (7 Aug 1957)

Phthalocyanine compounds containing a halogenotriazine ring—



(P = metal-free or stable metal phthalocyanine radical; Y = direct link or divalent bridging radical; P–Y contains ≮ 1 solubilising group; R = H, Alk, aralkyl or cycloalkyl; X = Hal; A = H or subst. or unsubst. hydrocarbon attached directly or through S to the triazine nucleus) are blue to green dyes of excellent wash fastness for cellulosic and nitrogenous fibres and for synthetic polymers such as polyamides. They are obtained by reacting an aminophthalocyanine P–$(YNHR)_n$ with a triazine (I)—

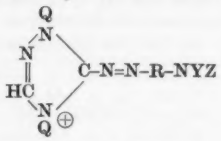


(B = X), or where Y = CO or COO, by reacting a phthalocyanine sulphonic or carboxylic acid chloride with an aminotriazine (I, B = NHR). Thus, Cu phthalocyanine-tetra-4-sulphonic acid is chlorsulphonated and the product condensed with 2,4-diaminobenzenesulphonic acid. The resultant Cu phthalocyanine-4-(*N*-3′-amino-4′-sulphophenyl)sulphonamide sulphonic acid is then condensed

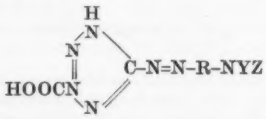
with cyanuric chloride to give Cu phthalocyanine-4-(*N*-3′-dichloro - s - triazinylamino - 4′ - sulphophenyl)sulphon - amidosulphonic acid, which is finally condensed with sodium thiophenol-*m*-sulphonate in an alkaline medium to give a dye which yields fast blues on cellulosic fibres. A.T.P.

Basic Diazacyanine Dyes
BASF *BP* 837,471 (Germany 14 June 1955)

The title compounds (I) have cations of formula—



(Q = Alk, aralkyl, cycloalkyl; R = *o*- or *p*-phenylene or naphthylene; Y and Z = H, subst. or unsubst. Alk, aralkyl, cycloalkyl, Ar or are members of a possibly subst. heterocyclic ring) and are clear red and bluish-red dyes for synthetic fibres (sec. acetate, *BP* 837,472) and compositions of polyamides, polyurethanes, polyesters, and polyacrylonitriles, tanned cotton, and lacquers. They are obtained from azo dyes—



(i.e. where diazo component is 3-amino-5-carboxy-1,2,4-triazole (II)) by decarboxylation in an organic solvent or aq. suspension at up to 200°c., and alkylation, which may be carried out simultaneously. Thus the dye from II and *N*,*N*-dimethylaniline is heated at 110°c. in dimethylformamide with dimethyl sulphate to give I where Q = Y = Z = CH_3, a clear red dye of good light and washing fastness on tanned cotton. I are bluer and are more water-soluble than the initial azo dyes and their colour is almost independent of the pH of their aq. or alc. solns. A.T.P.

Stabilised Phenylene Diamines
General Aniline *BP* 835,313 (U.S.A. 31 July 1956)

Phenylene diamines are stabilised to atmospheric oxidation, storage, heat, and light by presence of elemental sulphur or by distilling them from a mixture of elemental sulphur and the diamine. C.O.C.

Pigment Dispersions
General Aniline *USP* 2,907,670 (22 March 1957)

Dispersions suitable for use in colouring paper, textiles, plastics and, especially, latex paints, are obtained by milling an aqueous mixture of a pigment and a non-ionic dispersing agent at 60–100°c. until a well-kneading plastic mass is obtained. Preferably the pigment is used as a water press cake or pulp. This yields a product in which the pigment is extremely finely dispersed. C.O.C.

Carbon Black (C.I. Pigment Black 6 and 7)
Columbian Carbon Co. *BP* 834,634 (U.S.A. 11 July 1957)

In producing the pigment by dispersing a hydrocarbon in a stream of hot blast flame gases better control of temperature, volume, composition, and velocities of the hot gases supplied to the reaction chamber is possible if the blast flame gases are separately generated outside the reaction chamber and directed at high velocity into one end of the chamber and tangentially to its inner wall thus forming a hot swirling stream of hot gases. C.O.C.

Separating Carbon Black (C.I. Pigment Black 6 and 7) from Effluent Gas
N.V. de Bataafsche Petroleum *BP* 834,989 (Holland 26 Aug 1957)

Beaded Carbon Black (C.I. Pigment Black 6 and 7)
Columbian Carbon Co. *USP* 2,908,586 (6 Feb 1957)

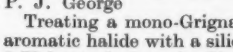
The pigment is first dry-beaded into beads of bulk density $\not<$ 20·5 lb./c.ft. Their outer surfaces are then wetted with water (40–90 lb. water/100 lb. pigment) and then dried to a moisture content of $\not>$ 1% by wt. This strengthens the outer surface of the beads and so reduces their tendency to crush, pack, and mat together under severe conditions of carriage and mechanical handling. The water is sprayed on to the beads so that the penetration does not exceed 25–33% of their diameter. During the spraying the beads are tumbled preferably with application of heat. They are dried by continued tumbling at $>$ 212°F. C.O.C.

Silica (C.I. Pigment White 27)
Columbia–Southern Chemical Corpn. *USP* 2,910,375 (13 July 1954)

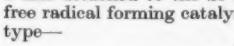
A product suitable for use with rubber and paper is obtained by treating calcium silicate of average particle size $<$ 1 μ. with aqueous NH_4Cl. C.O.C.

Fluorescent Organosilicon or Organotin Polymers
P. J. George *USP* 2,910,495 (17 Sept 1956)

Treating a mono-Grignard derivative of a difunctional aromatic halide with a silicon or tin halide having at least 2 Hal attached to the Si or Sn, in presence of a suitable free radical forming catalyst, so as to produce polymers of type—



or



yields products which fluoresce in ultraviolet radiation and which have excellent fastness to light and weathering when used in coating compositions. Thus *p*-dibromobenzene (24 parts) in ether (100 ml.) is treated with Mg turnings (24 parts) in ether (50 ml.). To the resulting Grignard solution are added dimethyldichlorosilane (13 parts) and cobaltous chloride (0·1 part). After reaction the mixture is refluxed for 12 hr., the ether distilled off and the residue heated with 5% HCl for 15 min. to remove the Co and Mg salts. The remaining solid is filtered off, washed with acetone and dried. The product is a yellow solid which does not melt at $<$ 300°c. and begins to turn brown when heated to $>$ 325°c. It is insoluble in acetone, alcohol, benzene, toluene, pyridine, chloroform, and glacial acetic acid. It has a brilliant greenish yellow fluorescence in ultraviolet radiation and retains this fluorescence even after heating with conc. H_2SO_4 at 100°c. C.O.C.

Polarography of Azo Dyes (XIV p. 524)

Coal-tar Colours. XXIII— D&C Red No. 19 (C.I. Basic Violet 10): Identification and Determination of Triethylrhodamine and 2-(2-Hydroxy-4-diethylaminobenzoyl)benzoic Acid in Commercial D&C Red No. 19 (XIV p. 524)

V— PAINTS; ENAMELS; INKS

The Rheology of Letterpress and Offset Inks
E. A. Apps *Research*, **13** (June 1960) 212–217

An account of the flow requirements and transfer properties of letterpress and offset inks and of the effect of water on the rheology of offset inks. 12 references. C.O.C.

Behaviour of Titanium Pigments in Industrial Finishes
W. Kampfer *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **32** (April 1960) 454–471

The properties of a titania (C.I. Pigment White 6) are fixed in its manufacture and can, in its application, only be developed. Gloss, opacity, and brightness of titania-containing industrial enamels are discussed as well as methods for enhancing these characteristics by proper formulation and vehicle selection. A simple method is described for the recognition of flocculation so that it may be treated where possible. Influence of vehicle combinations on gloss and brightness is described together with a basic method for formulation to give the optimal gloss, hiding, and cost level. J.W.D.

Amorphous Silica (C.I. Pigment White 27) in Clear Flatting Finishes
H. S. Ritter *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **32** (April 1960) 495–508

The mechanism by which fine particles cause flatting in clear finishes is reviewed and the properties of amorphous silicas used for this purpose are discussed. The performance of a commercial silica of this type, Hi-Sil X.303 (Columbia–Southern Chem. Corpn.), is described and

discussed; additional milling is required, as compared with a "stir-in" type of silica, but this is more than offset by lower cost. J.W.D.

Use of Ceramic Materials in Formulating Heat-resistant Paints
J. R. McKinnie *Off. Dig. Fed. Paint Varn. Prod. Cl.* **32** (April 1960) 472–485

Ceramic frit or "conversion coating" paints which are converted to ceramic enamels when heated strongly enough to destroy the organic binder, are described together with their uses. Potential fields of usage and limitations are also discussed. There are many references to the literature. J.W.D.

Polymers in Mixed Solvents
R. Noel and D. D. Patterson *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **32** (April 1960) 443–453

The intrinsic viscosities of polymer soln. in mixed solvents are treated in terms of polymer soln. thermodynamics. For two model systems at least, polyisobutylene–benzene–cyclohexane and polystyrene–benzene–cyclohexane, the theory of Guggenheim gives a better picture than that due to Flory. Solubility and the phenomena of cosolvency in mixed solvents and viscosities of conc. polymer soln. are also briefly discussed. J.W.D.

Water-thinned Semi-gloss Enamels Containing Tung Oil Resins
A. C. Richard and C. A. Murray *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **32** (April 1960) 509–518

Semigloss, water-thinned, emulsion paints of low pigment vol. concentration, in which the polyvinyl acetate copolymer emulsion was modified by the addition of an alkyd or epoxy ester emulsion to the extent of 20% of the vehicle solids, were prepared. Those modified with a tung–tall oil alkyd ester were superior in gloss, hardness, adhesion, abrasion- and scrub-resistance; the epoxy-modified paints had better colour retention. This enables the main defect of polyvinyl acetate paints, viz. poor water-resistance, to be overcome. J.W.D.

Recent Developments in Finishes Based on Water-dispersed Paint Systems
E. C. Scholl *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **32** (April 1960) 519–535

A review of the development in latex paint formulations for concrete floors, semi-gloss and gloss interior paints, roof paints, fire-retardant paints, and paints for exterior masonry and wood surfaces. J.W.D.

One-package Urethane Coatings
M. E. Bailey, G. C. Toone, G. R. Skreckoski, and G. S. Wooster *Off. Dig. Fed. Paint Varn. Prod. Cl.*, **32** (April 1960) 486–494

One-package urethane coatings having the shelf-life and ease of application of ordinary coating vehicles are produced by a process similar to that yielding alkyds, a diisocyanate replacing the dicarboxylic acid or anhydride. Exposure test results are excellent, but two-package urethane coatings have superior toughness and resistance to corrosive chemicals. J.W.D.

PATENTS

Printing Inks for Regenerated Cellulose Film
Kalle & Co. *BP* 833,829 (Germany 18 Jan 1957)

Addition of an organic polyisocyanate much improves the adhesion of printing inks to regenerated cellulose film. C.O.C.

Water-in-oil Emulsion Mimeograph Inks
Pakistan Council of Scientific and Industrial Research *BP* 834,311 (20 May 1957)

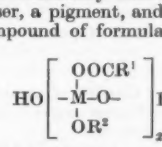
A pigment is dispersed in a mixture of a mineral oil, a drier, and a stabiliser obtained by heating rosin and mineral oil at 280–290°c. in presence of litharge until the mass when mixed with an equal volume of the same mineral oil has viscosity 400 cs. To the mixture there is added an aqueous solution of glycerol, cane sugar or molasses, the amount being such that there is 40–42% of water in the resulting ink. C.O.C.

Coloured Ink for Transfer Paper Yielding Coloured Impressions Suitable for Copying by Thermo-sensitive Processes
Caribonum *BP* 834,843 (19 June 1957)

Paper or other base is given a transferable coating containing graphite and a colorant. The graphite forms 15–20% by weight of the coating whose colour depends on the colorant used. Thus a coating for blue carbon paper consists of fatty grey carnauba wax (16–19% by wt.), petroleum jelly (14·34), mineral oil (8·00), blue resinate (1 part of Victoria Blue B Base (C.I. Solvent Blue 4) milled on a hot three-roll mill with 2 parts of rosin) (6·00), Strong Blue Lake (13·25), Ultramarine Blue (C.I. Pigment Blue 29) (12·43), China clay (C.I. Pigment White 19) (11·69), and graphite (C.I. Pigment Black 10) (18·04). Impressions made by this paper give good copies with thermo-sensitive copying processes. C.O.C.

Vinyl Chloride Resin Coating Composition
Union Carbide Corpn. *BP* 834,857 (U.S.A. 24 Dec 1957)

A coating composition of improved gloss and stoved colour retention comprises vinyl chloride polymer or a copolymer with an olefinically unsaturated compound, a solvent, a plasticiser, a pigment, and 0·5–5·0% (on wt. of pigment) of a compound of formula—



or $(R^1O)_y\,Q(OC_2H_4NR^2_2)_{4-y}$

or $(R^1O)_y\,Q(OC_2H_4NR^2_2)_{4-y}\cdot(HOOCR^3)_z$

or $(R^1O)_x\,M(OCH_2CH_2\cdot CR^4R^5R^6)_{4-x}$

(M = Si, Sn or Pb; Q = Si, Sn, Sr or Pb; R^1, R^2, and R^3 = same or different, Ar, alkaryl, aralkyl, Alk or subst. Alk of 10–18 C; R^4 = H, OH, or subst. or unsubst. Alk; R^5 = H or subst. or unsubst. Alk; R^6 = subst. or unsubst. hydroxyalkyl; $x = 1$, 2 or 3; $y = 0$, 1, 2 or 3), e.g. dibutoxy-di(triethanolamine)silicon-*NN*-dioleate. C.O.C.

Aluminium and Aluminium-based Paints and Their Analysis (IV p. 510)
X-Ray Study of the Interaction between Paper and Binding Constituents of Printing Inks (IX p. 521)

VI— FIBRES; YARNS; FABRICS

Physical Properties of Chemically Modified Cottons. Part V— Effects of Aminisation
A. W. McDonald, G. C. Humphreys, and J. N. Grant *Text. Research J.*, **30** (April 1960) 312–317

Yarns from six widely different cottons were aminised to a degree of substitution of about 0·043. They were allowed to contract in length during the chemical treatment but placed under a small load during washing and scouring. Regain and linear density were increased by the treatment. Modified cellulose density and fibre length were noted. Changes in tenacity and modulus showed inconsistencies among samples of different cottons, with trends similar to those found in mercerising. Decreases in tenacity occurred with fibre bundles but increases for the yarns. Single fibres showed no appreciable changes in tenacity. Secant moduli of fibres and yarns were in between those of slack and normal length mercerisation. C.O.C.

Effect of Cellulose on Cotton Fibre Microstructure
B. R. Porter, J. H. Carra, V. W. Tripp, and M. L. Rollins

Part I— Degradation by Cellulose in Fungal Growth Filtrates
Text. Research J., **30** (April 1960) 249–258

The degradation observed under the electron microscope is explained as a hydrolytic attack on the cellulose chains. The attack occurs in isolated areas along the fibre axis, not identified with a known structural feature, and produces jagged transverse cracks which can be seen in both electron and optical micrographs. Continued enzymolysis produces etching, or pitting, of the surface of the macrofibrils and formation of small fragments which include some particles similar in appearance to hydrocellulose particles. More extensive and uniform etching

of macrofibrils and formation of hydrocellulose-like particles were seen with enzyme-degraded, mercerised, or fragmented fibres than are found in fragments of degraded, unmodified raw or scoured fibres.

Part II— Degradation During Growth of Cellulolytic Micro-organisms *Ibid.*, 259–267

Initial bacterial cellulolysis causes diagonal or longitudinal cracks on the fibre surface; fungal attack is characterised by an approximately transverse splitting of the surface and underlying structure. Damage to the macrofibrils within the secondary walls of the fibre is similar to but more intense than damage by growth filtrates. There is a continued breaking down of the fibrillar sheets of the secondary layers into small fragments and of these into small hydrocellulose-like particles. C.O.C.

The Effect of some Reactive Dyes on the Dimensional Stability of Wool Fibres Treated under Stress in Boiling Water

A. Vassiliadis J.S.D.C., **76** (June 1960) 355

Mechanical Properties of Feather and Down Fibres

J. H. Dusenbury, C.-N. Wu, and C. J. Dansizer

Part I— Measurements at 60% R.H. and 70°F.

Text. Research J., **30** (April 1960) 277–290

Part II— Design and Operation of a Vacuum Vibroscope

Ibid., 290–296

Radiation-induced Graft Copolymerisation of Methacrylic Acid to Nylon

R. Roberts and J. K. Thomas

J.S.D.C., **76** (June 1960) 342–344

The Acrylic Fibre ACSA and its Dyeing Properties

I. Ammacher *Melliand Textilber.*, **41** (May 1960) 577–579

This Italian-made fibre consists of 85% acrylonitrile and of 15% of other vinyl derivatives. For bleaching sodium chlorite is recommended and recipes are given. Different classes of dyes such as disperse, basic, acid, metal-complex, and chrome dyes can be used. A list of suitable dyes in each class is given together with fastness properties obtainable. W.M.

Russian and Satellite Research and Development in the Field of Synthetic Fibres

R. C. Laible and L. I. Weiner

Text. Research J., **30** (April 1960) 239–248

Man-made fibre developments in Russia and the countries controlled by Russia are reviewed and compared with those in Western Europe and the U.S.A. At least three Russian fibres— Enant, a nylon 7, Ftorlon, a fluorine-containing polymer, and Vinitron, a combination of nitrocellulose with chlorinated polyvinylchloride— have no equivalents in either the U.K. or the U.S.A. Other fibres, e.g. Nitron, Lavsan, Anid, Steelon, and Khlorin are so closely related to Orlon, Terylene, nylon 66, nylon 6, and PeCe fibre respectively that the degree of originality in their development cannot be ascertained. East German work on experimental fibres and the conjectural Latvian use of 2-methylpiperazine for preparation of new polymers show the possible contribution of the satellite countries to the total Russian effect. There is also a brief discussion of the position of research on new fibres in Russia indicating the increased effort that may be expected from Russian research and development workers in the future. 44 references. C.O.C.

PATENTS

Cellulose Thiourethanes

American Viscose Corpn. *USP* 2,910,466 (6 Feb 1956)

Viscose is treated with dilute acid to reduce its free alkali content and then with an aqueous solution of a salt of a di- or tri-valent metal which forms a complex with the viscose. The complex obtained is treated directly with a primary or secondary amine for several hours to produce the cellulose thiourethane. This is then separated, washed, and if desired treated with acid to convert residual xanthate groups to hydroxyl groups. Cellulose thiourethane can be spun into filaments which are readily dyed with dyes having affinity for wool. C.O.C.

Poly(vinyl Alcohol) Fibres of Improved Dye Affinity

Air Reduction Co. and Kurashiki Rayon Co.

USP 2,906,594 (30 March 1956)

Fibres consisting of oriented poly(vinyl alcohol)-poly(vinyl nonamino-acetal) and poly(vinyl alcohol)-poly(vinyl nonamino-acetal)-poly(vinyl amino-acetal), there being $< 30\%$ by wt. of the first component, have good affinity for acid and mordant dyes and resistance to boiling water. 0·2–10·0% of the total OH groups present are acetalised by an amino-aldehyde and 5–60% by a nonamino-aldehyde. C.O.C.

Partly Acetylated Poly(vinyl Alcohol) Fibres

Mitsubishi Rayon Co. *BP* 834,612 (20 Dec 1957)

Poly(vinyl alcohol) containing unsaponified acetyl groups comprising $> 0{\cdot}5\%$ of the alcohol, is heated while solid and then partly acetylated in a heterogeneous system with various aldehydes or their acetals. The product while still soluble in hot water is extruded into filaments, stretched, heat set, and then further acetylated. This results in production of fibres of good resistance to boiling water or water in a sealed tube at $> 100°$C. C.O.C.

Mass Coloration of Vinyl Polymers

Ciba *BP* 834,580 (Switzerland 4 Aug 1955)

A metalliferous monoazo dye free from sulphonic groups and containing no carboxylic groups other than in *ortho* position to the azo linkage is added to the polymer before it is worked up. The process is particularly suitable for the preparation of mass-coloured acrylic fibres. C.O.C.

Modified Artificial Fibres and Films

DuP *USP* 2,908,659 (6 Aug 1953)

Controlled modification of artificial fibres and films is accomplished without adverse effect on their mechanical or physical properties when heated by incorporating into them a "d-microgel". A d-microgel is unimolecular colloidal particles of a cross-linked polymer of average diameter 0·01–3·01 μ. cross-linked to such an extent that it forms a microsol when extruded in liquids in which it is swellable and shows in such liquids a definite gel point. The microsol has properties of both true dispersions and true solutions and its viscosity has no relationship with molecular weight. The gel point is the concentration at which the microgel absorbs the extruding medium. 18 examples of such microgels are given and their use described in 13 examples. They are added to the spinning solution and can be used to improve the dyeing properties of the resulting fibres or films. C.O.C.

Constitution and Properties of Surfactants. II— Sorption of Anionic Surfactants on Fibres (III p. 504)

Modifying Fibres or Films of Natural or Regenerated Natural Polymers (X p. 522)

VII— DESIZING; SCOURING; CARBONISING; BLEACHING

Desizing with Sodium Bromite

R. Freytag *Teintex*, **25** (May 1960) 323–337

Treatment is cold and thus regular and reproducible. Penetration is claimed to be better because of the absence of swelling. The goods can be kiered without rinsing. Consumption is of the order of 1 g. active Br per kg. of sized textile. S.R.C.

PATENTS

Solvent Scouring of Wool

Agency of Industrial Science and Technology, Ministry of International Trade and Industry (Japan)

BP 835,502 (28 Jan 1958)

The raw wool is passed through several baths of organic solvents. Some of the grease-containing solvent from each except the first bath is added to the solvent in the preceding bath, the proportion so used depending on the grease content of the wool. Fresh solvent is supplied to the last bath. The wool is squeezed between each bath. The solvent left in the scoured wool is recovered. C.O.C.

Chlorite Bleaching with Simultaneous Desizing

Kalle & Co. *BP* 833,914 (Germany 20 July 1957)

Enzymatic desizing agents active in neutral liquors at $< 60°$C. and substances yielding acid only at $> 60°$C. are added to a neutral chlorite bleaching liquor. Cloth is first impregnated with the cold liquor and then heated to $> 60°$C. Thus cotton cloth sized with farina is impregnated at 20–40°C. with its own weight of an aqueous solution containing $(NH_4)_2SO_4$ (10 g./l.), non-ionic wetting agent (5), Na chlorite (15), and pancreas amylase (20

Willstätter amylase units) (10), and then heated at 75–98°C. for 60 min. It is then neutralised at 90°C. and dried. This yields an almost complete bleach and good desizing. C.O.C.

VIII— DYEING

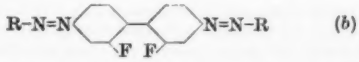
Relationship between Structure, Particle Size in Solution and Speed of Diffusion, into Cellulosic Fibres of some Direct Dyes

B. N. Mel'nikov, B. M. Krasovitskiĭ, and P. V. Morÿganov
Tekhnol. tekstil. prom., No. 1 (14) (1960) 111–120

The diffusion coefficient in cuprammonium staple fibre and in solution together with the particle size were calculated for a series of direct dyes having regular changes in their structure. For measuring diffusion into fibres 0·05 g./l. dye was used at 50 and 70°C. Diffusion in solution was investigated using 0·1 g./l. dye at 25° and 40°C. In each case 10 g./l. of electrolyte (NaCl) was used. Breaking of conjugation by introduction of suitable chromophoric blocks (CH_3 or CONH) will (*a*) increase diffusion of dye into the fibre, (*b*) decrease aggregation in solution, (*c*) decrease adsorption of dye by cellulose. It is possible to prepare dyes of formula—

(*a*)

or



(*b*)

which will have a high rate of diffusion within the fibre, low degree of aggregation and will be readily absorbed by the fibre. In (*b*) substituting Cl or CH_3 for F gave increase in rate of diffusion with a drop in affinity. Introduction of > 1 CONH group in the dye molecule increases affinity for the fibre but decreases the rate of diffusion. Introduction of pyridine into the dyebath will in most cases decrease aggregation. With dyes not forming large aggregates addition of pyridine causes increase in particle size. Pyridine also increases the rate of diffusion into the fibre. L.S.L.

New One-bath Method for Continuous or Pad-Roll Vat Dyeing

F. L. J. van Lamoen and H. Borsten
J.S.D.C., **76** (June 1960) 349–354

Reactive Dyes on Cellulose

E. Elöd and Y. Nakahara
Melliand Textilber., **41** (May 1960) 567–572

Kinetic studies of the desorption of reactive dyes dyed on cellulose indicate that a first order chemical reaction between dye and fibre takes place. Dyes having two reactive Cl atoms per molecule can— depending on temperature and alkalinity— react in 3 different ways with cellulose. The solubility in cuprammonium of cellulose dyed with reactive dyes varies with the conditions of dyeing. W.M.

Dyeing Methods for Mixtures of Polyester and Cellulose Fibres

F. H. Robaard *Mededeling van het Vezelinstituut T.N.O.* No. 117 (April 1959) (49 pp.)

A review of the literature covering: properties of polyester fibres; principles of dyeing; dyeing of polyester fibres (disperse, azoic, vat, and other dyes); pre- and after-treatments (desizing, scouring, bleaching, heat setting, anti-pilling, and treatment with caustic); processing of polyester fibre–cellulose blends; stripping; finishing. 76 references. R.A.

Dyeing of Wool by Solvent-assisted Processes

W. Beal, K. Dickinson, and E. Bellhouse
J.S.D.C., **76** (June 1960) 333–341

One Bath Dyeing of Silk with Chrome Dyes— Part 3

Sh. Kh. Averbukh and M. K. Lepetkova
Tekhnol. tekstil. prom., 1 (14) (1960) 121–128

The economic advantages of the method are stressed. Dyes having affinity from acid baths are recommended. Optimum dyeing pH (2·5) is obtained with formic acid which at the same time protects the fibre from damage caused by oxidation. During dyeing the dye is absorbed first, the bichromate remaining in solution. This prevents lake formation outside the fibre. The quantity of bichromate recommended is 100–133% on the weight of pure dye. L.S.L.

Dyeing of Synthetic Fibres
III— Effect of Temperature of Drying on the Properties of Nitron Acrylic Fibre

A. A. Kharkharov and G. A. Arestova
Tekhnol. tekstil. prom., No. 1 (8) (1959) 137–140

Dependence of dye uptake of Nitron upon initial drying temp. (0–110°C.) using disperse (Bordeaux 2C) and direct (Sky Blue) dyes has been investigated. It is found that 70°C. is a critical temp., above which dye absorption decreases rapidly. This is attributed to removal of hydrogen-bonded water molecules between neighbouring polymer chains. The effect of final moisture content of the fibre is not appreciable, best results being obtained at 6–8% moisture content with disperse dyes and 12–15% with direct dyes.

IV— Dyeing Capron with Vat Dyes

V. F. Androsov and A. A. Kharkharov
Ibid., No. 2 (9) (1959) 110–116

The effects of dyebath, temp., acid nature, addition of urea as antioxidant, dichromate development, and of the degree of deamination of capron on its dyeing properties with solubilised vat dyes have been investigated. Fastness properties of two dyes are given, showing poor fastness to light.

VIII— Diffusion Properties of Vat Leuco Esters in Capron

V. F. Androsov and A. A. Kharkharov
Ibid., No. 2 (15) (1960) 97–100

The diffusion coefficients (I) have been determined of two leuco esters of vat dyes for capron (fibre and film) under varying electrolyte concn. and temp. conditions (30–90°C.). On introduction of auxiliary dispersing agents into the dyebath I increased and passed through a maximum. G.J.K.

Dyeing of Nitron Acrylic Fibre for Carpet Yarn

Z. I. Kurokhtina *Tekstil. prom.*, **19** (Oct 1959) 72

Carpet yarn composed of 70% cuprammonium and 30% Nitron wears satisfactorily. Nitron is dyed with acid dyes, using the cuprous ion technique, giving good fastness to light and to wet and dry rubbing but lighter dyeings compared with other fibres under identical conditions. Dyeing recipe for a five-coloured carpet is given. G.J.K.

Heats of Solution of Dyes in Water and the Problem of Dyeing

S. M. Lipatov and I. M. Movchovich
Kolloid. zhur., **21** (Sept–Oct 1959) 522–525

Temp. dependence (20–90°C.) of heats of soln. of Congo Red (I) and Direct Sky Blue (II) in water, 1% NaCl, 20% pyridine, 20% (for I and II) and 80% (for II) ethanol soln. has been investigated and found to be appreciably different for the two dyes. With Congo Red, there is a sharp decrease in the heat of solution between 60–75°C. in all solvents, whilst II shows gradual decrease over the entire temp. interval. Using 8 direct dyes, it is shown that ΔH° and ΔS° characterise fibre and dye reactivity better than $\Delta\mu^\circ$. G.J.K.

Dyeing Furs Brown

A. I. Levchenko
Kozhevenno-Obuvnaya Prom. (7) (1959) 20–22
Chem. Abs., **54** (25 March 1960) 6133

The furs are soaked for 1 hr. in a 5–10% ammoniacal solution of 2,7-dihydroxy-1,4-naphthoquinone at 40–50°C., then for 30 min. in the same bath after addition of acetic or hydrochloric acid, and finally rinsed and dried. They are then treated for 30–60 min. in a solution of an azoic diazo component so as to form an insoluble azo dye on the fibres. Chrome compounds remaining from tanning promote level dyeing and fastness to washing. C.O.C.

Dyeing Sheepskins Dark Blue, Black or Brown

A. M. Rodionov
Kozhevenno-Obuvnaya Prom., (7) (1959) 18–20
Chem. Abs., **54** (25 March 1960) 6133

Sheepskins are treated with a 5·6 g./l. solution of 1-amino-8-naphthol-3,6-disulphonic acid at 38–40°C., and pH 2·0–2·7 for 3 hr., rinsed, and then coupled with diazotised 4-amino-4'-methoxydiphenylamine for 2 hr. at 30–35°C. and pH 7·5–8·5. Finally they are rinsed and

treated with acidic $K_2Cr_2O_7$. This yields dark blue to black dyeings. If the skin is treated with aqueous solution of $NaNO_2$ (2·5 g./l.) and HCl or H_2SO_4 (6 g./l.) for 6 hr. at 15–20°c. the hair is diazotised. Subsequent treatment with *m*-phenylenediamine or 1-naphthylamine (2·5 g./l.) for 15 min. at 15–20°c. produces a brown. C.O.C.

Dyeing and Finishing in the Hatting Industry
B. Kramrisch *J. Textile Inst.*, **51** (April 1960) P 191–P 199

The dyeing machinery and classes of dyes used for wool and fur felts in both semi-planked and fully-planked states are discussed in the light of practical experience. Dependence of fastness both on depth of dyeing and on class of dye used is illustrated by several examples. Use of synthetic fibres, regenerated cellulose fibres, and bast fibres in the hatting industry is briefly mentioned. Chemical finishes are, in general, less important than the mechanical finishes, but hand proofing with fat improves lustre and firmness can be improved with shellac and borax. S.B.D.

Current Views on the Mechanism of Leather Dyeing
G. Otto *Leder u. Häutemarkt tech. Beilage*, **11** (1959) 297

A review article having sections devoted to the properties of polypeptide fibres, ionic nature of water-soluble dyes, different types of amphoteric dyes, dye adsorption as a function of pH, titration curves of acid, and free dye acids for wool and hide substance, relationship between dye constitution and affinity, affinity and aromatic nature, rôle of conjugated bonds, aromatic properties, dipoles, tautomerism of the peptide group, influence of the ionic groups on the co-ordination affinity of dyes, changes in isoelectric point and surface potential produced by collagen tanning, reactions between anionic dyes and chromic hydroxide, dyeing behaviour as a function of dye constitution, dyeing properties as a function of the chrome compounds present in leather, changes in the dyeing properties produced by drying chrome leather, range of forces and phases of combination, and the main rules governing dyeing. The text is similar to the author's BASF Monograph having the same title, figures, and tables. C.O.C.

PATENTS

Dyeing Textiles on Forms
Bellfour Ges. für Verfahrens -und Trocknungstechnik
BP 833,773 (Germany 19 Dec 1955)

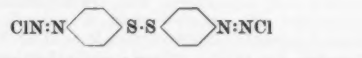
The textiles on forms are placed in the dye vessel and a small quantity of dye liquor is collected below them and fed to a pump which circulates it over the forms. The necessary temperature and pressure are produced by steam injection into the dyeing vessel. The dye vessel is closed so that the liquor may be at > 100°c. thus enabling dyeing and setting to occur simultaneously. C.O.C.

Vat or Sulphur Dyeing
BASF *BP* 834,393 (Germany 10 July 1957)

Compounds containing several lactam groups with 5–7 members in the lactam ring and having between any two lactam groups a C chain one end of which is linked to the N atom of a lactam group, this chain containing S and/or N and having 2–6 C between each lactam group and the adjacent hetero atom, e.g. condensate of 1 mol. triethylene tetramine and 2 mol. butyrolactone, are excellent levelling agents for use in vat and sulphur dye-baths. C.O.C.

Dyeing Animal Fibres with Azo Dyes containing a Disulphide Bond
Société Monsavon l'Oreal
BP 833,809 (France 17 July 1956)

Animal fibres, especially live human hair, dye readily in an aqueous solution at pH 7–11 of an azo dye having at least one disulphide bond and an aliphatic mercapto-carboxylic acid, thiourea dioxide (C.I. Reducing Agent 11), alkali metal borohydride, sulphite or hydrosulphite. Thus the dye—



dyes white hair brownish orange in presence of ammonium thioglycollate and ammonia. On treatment with H_2O_2 the dyed hair turns orange. C.O.C.

Prevention of "O-fading"
Celanese Corpn. of America
BP 835,430 (U.S.A. 14 Sept 1955)

Incorporation of a compound containing no N atom but having aliphatic carbon to carbon unsaturation, e.g. a linear polyester of ethylene glycol with methallyl succinic acid, reduces the O-fading of dyeings on cellulose esters. A gas-fading inhibitor, e.g. poly(methylvinyl-pyridine), may also be present. The fibres containing these inhibitors have reduced tendency to discolour when heated, compared with those containing amine-type inhibitors. C.O.C.

Dyeing Polyurethane Foam
ICI *BP* 834,321 (5 July 1957)

Even dyeing is obtained by conventional methods when the volume of the dyebath is 75–100% of that of the air space in the polyurethane foam. C.O.C.

Colouring Aluminium and its Alloys Green
High Duty Alloys *BP* 834,049 (16 May 1957)

The aluminium is anodised in sulphuric, oxalic, malonic sulphamic or chromic acid and then treated in an aqueous solution of a copper salt or complex. After being rinsed in water it is then treated with an aqueous solution of an inorganic sulphide, H_2S or a S-containing organic compound decomposing in presence of Cu ions. Finally it is treated in a sealing bath at pH 5–6 or is steamed. The green produced has excellent fastness to light. C.O.C.

Constitution and Properties of Surfactants. II— Sorption of Anionic Surfactants on Fibres (III p. 504)
Solvent Dyeing of Azoic Dyes on Polyester Fibres (IV p. 513)
The Effect of some Reactive Dyes on the Dimensional Stability of Wool Fibres Treated under Stress in Boiling Water (VI p. 518)
The Acrylic Fibre ACSA and its Dyeing Properties (VI p. 518)
Mass Coloration of Vinyl Polymers (VI p. 518)
The Electro-fixer, its Design and Possibilities of Application (IX below)
Pigment Dyes in the Textile Industry (IX p. 521)
Clear and Pigmented Oil-in-water Emulsions for Dyeing and Printing Textiles (IX p. 521)

IX— PRINTING

The Origins of English Calico Printing
P. C. Floud J.S.D.C., **76** (May 1960) 275–281

The English Contribution to the Early History of Indigo Printing
P. C. Floud J.S.D.C., **76** (June 1960) 344–349

New Developments in the Printing of Vat Dyes
A. Blum *Melliand Textilber.*, **41** (May 1960) 587–593

Difficulties are sometimes encountered in the steaming of vat prints if Rongalit C (C.I. Reducing Agent 2) is used as reducing agent and these difficulties can become especially serious in screen printing, where print pastes of higher stability than those prepared with Rongalit C are required. A new reducing agent of higher stability is now available under the name of Rongalit FD. Print pastes with the new agent keep much better but longer steaming times are, however, needed. The new product is also recommended for use with vat dyes which are liable to over-reduction. Another new reducing agent is Rongal A which is claimed to be especially suitable for the "two phase"-(Colloresin) process. It is quick acting and steaming times of only 30 sec. suffice. W.M.

The Electro-fixer, its Design and Possibilities of Application
H. Aubauer *Melliand Textilber.*, **41** (May 1960) 600–605

This machine was originally developed for use with the "two-phase" printing process for vat dyes (Colloresin process). The basic idea is that only at the start of fixing is a small amount of steam used to expel the air and heat the goods. The heat required for complete reduction and fixation of the vat dyes is supplied by electricity. It is found that decomposition of the reducing agent can be much better controlled in the electro-fixer than in an ordinary steamer. The machine can be used to fix pigments. A modified type of the electro-fixer can be used for the pad dyeing of vat dyes. W.M.

Pigment Printing using a Polyvinyl Acetate Binder
G. I. Shilova

Tekhnol. tekstil. prom., No. 1 (14) (1960) 133–136

Several printing recipes based on mixtures of thermoplastic and thermosetting resins have been developed, e.g. of paste: Preparation OP10 (1 g.), [$C_8H_{17}C_6H_4$-$O(CH_2$-CH_2-$O)_{(10-13)}$-CH_2CH_2OH], 60% polyvinyl acetate emulsion (40), white spirit (32), ammonia (20%) (1), thermosetting resin (10), dibutyl phthalate (15%) (10), ammonium thiocyanate (1), and phthalocyanine blue (C.I. Pigment Blue 15) (21%) (5). After printing the fabric was dried and cured at 104–108°C. for 8–10 min. or at 130°C. for 1 min. Resultant prints had excellent all round fastness. The printing pastes were of the "oil in water" type and were readily removed when the machine was cleansed. L.S.L.

New Horizons in Pigment Printing
N. S. Cassel

Amer. Dyestuff Rep., **49** (21 March 1960) 35–40

The importance of surface tension in the preparation of water-in-oil and oil-in-water emulsions is explained and the characteristics of the 2 types discussed. The desirable properties of a pigment (colour value, covering power, brilliance) are described and the problems of the fastness properties of pigment prints reviewed. The degree of adhesion between fibre and resin is responsible for wash fastness, and adhesion is assumed to depend on polar groups present in the fibre and resin. The same polar groups attract water and decrease their wash fastness. The alkydamine resins are, however, crosslinked on thermosetting and the polar groups lose their reactivity with water. Fastness to rubbing is the most serious problem. Considerable improvement was obtained by addition of elastomers. For fastness to wet rubbing the binder should not contain any substances sensitive to water. The requirements a binder for pigment printing should fulfil are listed. Polar groups give good adhesion, and the binder must retain its elastomeric properties after condensation. Polar groups on the binder should be tied up so as to lose reactivity with water. A reactive agent must be present capable of tying up all polar groups on all ingredients to make the binder after condensation highly resistant to water. The best results were obtained with emulsion polymers. This technique allows the use of a combination of monomers and makes it possible to impart the desired properties to the final polymer. A reactive agent (see above) has been found which reacts not only with all the ingredients but probably with the fibre as well. Though an ideal solution has not yet been found confidence is expressed that the new concept of the binder will help to develop pigment printing beyond its present limitations. W.M.

Pigment Dyes in the Textile Industry
G. Weekler *Melliand Textilber.*, **41** (May 1960) 573–576

Advantages and disadvantages of the use of pigment dyes for the dyeing and printing of textiles are surveyed. The importance of the thickener is explained and properties of oil-in-water and water-in-oil emulsions are discussed. Desirable properties of pigment dyes are listed and the suitability of a number of inorganic pigments is considered. W.M.

X-Ray Study of the Interaction between Paper and Binding Constituents of Printing Inks
M. P. Volarovich, V. T. Ivanova, E. M. Afanas'eva, and K. F. Gusev *Kolloid. zhur.*, **21** (Sept–Oct 1959) 544–551

Interaction of ash-free filter paper (FP) with starch (I), gelatin (II), drying oil (III), and petroleum jelly (IV) was investigated by X-ray diffraction technique (Cu K; camera radius 80 mm.). It showed that the paper had a monoclinic unit cell ($a = 8{\cdot}78$, $b = 10{\cdot}3$, $c = 7{\cdot}96$ A.; $\beta = 84°$). Impregnation of the paper with I or sizing with II caused some disorientation of cellulose chains in the planes (101) and $(10\bar{1})$ and lattice expansion in the plane (002) by 1·5–2%, this effect being absent in paper treated with IV. On the other hand, impregnation with III caused redistribution of the intensities of interference max. of (200) and (002) and formation of intermediate forms of cellulose structure similar to those encountered in mercerised cellulose. Occurrence of chemical interaction between the paper and drying oil was confirmed chemically using the saponification-number technique. G.J.K.

PATENTS

Textile Printing
British Tufting Machinery *BP* 834,123 (15 Nov 1956)

Apparatus for printing on pile fabrics, felts, towels and raised fabrics and for warp printing comprises at least one printing roller having a pattern in relief formed by resilient cellular material. Colouring composition is supplied to the cellular material which is subjected to pressure when it contacts the fabric or warp to be printed so that the colouring composition is transferred to the latter. This results in prints which penetrate through to the bottom of the pile without spreading beyond the edges of the desired pattern. C.O.C.

Printing with Vat Dyes Dispersed in a Water-in-oil Emulsion
DuP *USP* 2,907,624 (5 Aug 1957)

A normal vat dye paste containing a small amount of a dispersing agent is emulsified into a water-in-oil emulsion previously formed by adding water to a water-immiscible hydrocarbon solvent containing a small amount of a resin dissolved and/or colloidally dispersed in it. The resulting printing paste is applied in the conventional manner by shallow-engraved intaglio rollers which may be run faster than when aqueous thickened vat dye pastes are used. The prints are then impregnated with caustic alkali and sodium hydrosulphite and led into air-free steam at 212–290°F. for 7–30 sec. The resin is at least in part, and usually completely, removed during the final soaping and washing off. This yields sharp prints as fast to light, washing, and rubbing as conventional prints but in many cases with double the colour value. C.O.C.

Clear and Pigmented Oil-in-water Emulsions for Dyeing and Printing Textiles
Gy *USP* 2,907,720 (23 July 1956)

Use of fatty acid ester resin binders which are emulsion polymerised or emulsion aggregated results in quicker solidifying binders, increased toughness and better ageing qualities of the resulting prints.

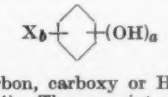
USP 2,907,721 (14 June 1954)

The binder used consists of an organic solvent-soluble amino-aldehyde resin and an alkyd resin containing (*a*) 50–100% of a pentaerythritol on the total wt. of polyhydric alcohol component, (*b*) a polybasic acid, and (*c*) a poly-unsaturated fatty acid. The latter forms 50–65% of the alkyd resin. C.O.C.

Printing with Acid Dyes on Acrylic Fibres
Deering Milliken Research Corpn.

USP 2,906,590 (5 May 1954)

The paste used contains an acid dye, a cupric salt, and a compound of formula—



(X = H, hydrocarbon, carboxy or Hal; $a = 1$–3; $b = 1$ or 2; $a + b = < 4$). Thus a mixture of Roracyl Dark Green B (40 parts by wt.), Du Pont Orange RO (7), Anthraquinone Blue SWF Conc. 150% (C.I. Acid Blue 25) (10), *p*-phenylene diamine (25), glycerin (25), and 6% aqueous gum tragacanth (150) is added to $CuSO_4$ (75) dissolved in water (500). The whole is then vigorously boiled for 45 min. Acrylic fibre fabric is then printed with this paste so that the printed portions of the fabric receive their own weight of dye. The printed fabric is dried, steamed for 3 min., scoured, and dried. This yields black prints of excellent fastness to light and washing. C.O.C.

Printing and Photography
J. F. Crosfield *BP* 834,125 (28 Nov 1956)

An electro-optical scanning system for comparing a copy with the original or a standard copy. C.O.C.

Photographic Colour Developer
Kodak *BP* 841,186 (U.S.A. 29 July 1957)

A mixture of a primary aromatic amino developing agent and n-octyl alcohol or a *p*-alkyl phenol (Alk of 1–5 C) results in dye images which are denser than those yielded by the developing agent in absence of the alcohol or phenol. It is especially useful with emulsions containing the colour couplers described in *BP* 541,589 and 791,219 (J.S.D.C., **74** (1958) 500). C.O.C.

Lithographic Transfer Sheets
W. Ritzerfeld and G. Ritzerfeld
BP 833,945 (Germany 15 March 1957)

Vesicular Prints
General Aniline *USP* 2,908,572 (28 Dec 1955)
Vesicular print material of high printing speed is obtained by coating a base with an aqueous solution of a hydrophilic colloid having dispersed in it a little of a finely divided solid together with a stabilised photosensitive diazonium compound and drying. The solid has the same refractive index as the colloid. After exposure to light the layer contains a latent image which is developed by short exposure to steam or heat. The visible image is fixed by drying or cooling to harden the colloid. C.O.C.

Scanning System for Use in Colour Reproduction
J. F. Crosfield *BP* 835,111 (24 April 1956)
A method of colour correction when producing separation negatives or positives. C.O.C.

Printing on the Tips of Pleats of Pleated Fabrics (I p. 503)
Mechanism of Dye Formation in Colour Photography. VII— Intermediate Bases in the Deamination of Quinonediimines (IV p. 509)
Reactive Dyes on Cellulose (VIII p. 519)
Colour Changes in Polymers by Irradiation (XIII p. 523)

X— SIZING AND FINISHING

Wash-fast Finish on Cotton Fabrics using Colloidal Solutions of Melamine–Formaldehyde Resins
P. V. Morÿganov, B. N. Mel'nikov, S. I. Kudryavtsev and R. S. Ovchinnikova
Tekhnol. tekstil. prom., No. 2 (15) (1960) 91–96
Colloidal soln. of the methyl esters of penta- and hexamethylol melamine, prepared with acetic acid, have been used to give wash-fast finishes on cotton fabrics by padding and drying twice over cylinders to polymerise the resin; heating for 2–3 min. at 100°c. being quite sufficient. There is no loss in tensile strength, the lustre of the original fabric is retained after washing, and the fastness to rubbing of sulphur dyes is improved. G.J.K.

Influence of Sonic and Ultrasonic Waves on Certain Finishing Processes
V. F. Androsov and A. A. Kharkharov
Tekhnol. tekstil. prom., No. 1 (14) (1960) 129–132
Samples of cotton fabric were given a standard finishing treatment, i.e. kier boiling, bleaching, and dyeing, while being subjected to sound waves of frequency 0·1 kc./sec. The effect of the sound waves is to increase the capillarity of the cloth: 120 cm. in 30 min. against 100 cm. in 30 min. with control samples. Fabric dyed in presence of sound waves absorbed 2·14 times as much of a direct blue. The sound waves decrease the degree of aggregation and increase the diffusion of dye into fabric. They have no influence on the rate of dyeing of Nitron with direct dyes, but using ultrasonic vibration (24 kc./sec.) slight increase in the rate of dyeing was observed. L.S.L.

The Padding Mangle
B. Giacomo *Tinctoria*, **57** (April 1960) 139–145
A detailed discussion of the factors determining the amount of colour taken up by a fabric when passing through padding mangle, viz. (1) bath, (2) degree of expression, (3) absorption by the fabric (preferential absorption of water or dye). The effects of temperature and viscosity of the bath and of the addition of surface-active substances on the amount of dye taken up are explained. The properties of the fabric which influence the "pick-up" are then considered. Finally the details of the design of the padding mangle which are of importance in this connection such as: pressure, curvature of the bowls, dimensions of the bowls, hardness of the material with which the bowls are covered, are discussed. W.M.

Dimensional Stability of Plain-knit Fabrics
D. L. Munden
J. Textile Inst., **51** (April 1960) P 200–P 209
The dimensions of any relaxed plain-knit fabric are determined by the length of yarn in the stitch and the number of stitches and courses in the fabric. The strains induced in a fabric during manufacture and finishing result in two main forms of shrinking. The first is relaxation shrinkage obtained when fabrics are immersed statically in water, and the second is consolidation shrinkage caused by the gradual return of fabrics to the stable wet-relaxed shape during washing after distortion by wet finishing or if they were unable to reach it by static wet-relaxation. Wool fabrics often show a third form of shrinking during washing, this is felting which can produce considerable area shrinkage without change in yarn length per stitch. S.B.D.

PATENTS

Treating Resin-treated Yarns
Permatwist Co. *BP* 834,551 (U.S.A. 21 Feb 1955)
Yarn previously treated with a thermoplastic or thermosetting resin is drawn at constant tension through a zone kept at or above the softening or curing temperature of the resin and allowing the yarn to cool before winding it. The supply of heat to the hot zone is automatically regulated so as to uniformly heat the yarn to the desired temperature and to maintain pre-determined concentration between applied tension and the contractile force of the yarn.

BP 834,552 (U.S.A. 21 Feb 1955)
Modification of *BP* 803,105. Thermoplastic yarn is twisted and then drawn at constant tension through a hot zone whose temperature is automatically regulated to enable the molecules of the yarn substance to adapt themselves to the twisted formation of the yarn. The yarn then passes through a cooling zone to set it. The tension applied is sufficient to prevent ductility in the finished yarn. C.O.C.

Modifying Fibres or Films of Natural or Regenerated Natural Polymers
DuP *BP* 834,557 (U.S.A. 7 April 1955)
The fibres or films are subjected to ionising radiation while they are in intimate contact with at least one organic compound which when chemically bonded (as such or as a polymer) with them as a result of the irradiation causes appreciable change in at least one of their properties. Thus wool cloth is impregnated with a 6% aqueous solution of poly(ethylene glycol) mol.wt. 20,000. The wet cloth is enclosed in an aluminium foil or wrapper and subjected to electron irradiation in a 1 Mev. resonant transformer with a beam-out current of 560 microamp. The sample is placed on a conveyor belt which takes it through the electron beam at 16 in. per min. The sample is traversed back and forth across the beam until a total dose of 40 Mrep. is attained. After 15 successive washings the irradiated sample retains its original dimensions and handle without unravelling at the edges. A control sample unravels and pills badly. C.O.C.

Soil Resistant Finish on Regenerated Cellulose
American Viscose Corpn.
BP 833,284 (U.S.A. 31 May 1956)
The fibres are treated with an aqueous suspension of grown silica particles to which, before growth, has been added a small amount of a non-basic salt of a multivalent metal. Thus aqueous solutions of colloidal SiO_2 (average particle size 18 mμ.) (0·05–0·15%) and aluminium sulphate (0·05–0·15 as $Al_2(SO_4)_3 \cdot 18H_2O$) were mixed and then aged for 3 hr. before being used to produce a soil-resistant finish on viscose staple fibre by treating it for 10 min. in the suspension using a liquor ratio of 20 : 1. Subsequent dyeing leaves enough SiO_2 on the fibres to impart a distinct soil resistant finish. C.O.C.

Alginic Acid Derivatives as Fire Resisting Agents
Deutsche Erdoel *USP* 2,907,683 (8 Feb 1954)
Textiles of all types are impregnated with an aqueous solution of a derivative of alginic acid, e.g. Na alginate, and are then treated to insolubilise the alginic acid derivative, e.g. by treatment with $CaCl_2$. C.O.C.

Cyanoethylation of Cellulose
American Cyanamid Co. *USP* 2,907,625 (8 March 1956)
Cotton is rendered highly resistant to microbiological attack by treating it with 75–150% of its own weight of 7–12% caustic soda lye and 5–10 times its weight of acrylonitrile at < 45°c. This enables cyanoethylation to be carried out in package dyeing machines. The AN ratio (acrylonitrile lost in side reactions/acrylonitrile reacted with the cotton) is about 1·2, i.e. much less than has hitherto been practical. C.O.C.

Flame- and Crease-resistant Textiles from Aziridine Carboxyalkylcellulose

U.S. Secretary of Agriculture

USP 2,906,592 (20 Aug 1957)

Compounds containing two or more 1-aziridinyl groups attached directly to P react with cellulose containing several carboxylic acid groups to produce chemically modified, flame- and crease-resistant textiles. Thus Na carboxymethylcellulose cloth containing 1 carboxy group per 15 anhydroglucose units was soaked for 5 min. in dil. HCl, rinsed in water, and air dried to yield the free acid form. It was then padded with a solution containing tris(1-aziridinyl)phosphine sulphide (5) and water (22) to 62·5% wet pickup. It was then heated for 5 min. at 90°C., washed in hot water and dried. Increase in weight was 8·2%. The fabric passed the 100° angle in the strip flame test. C.O.C.

Stiffening Poly(ethylene Terephthalate) Fabrics

Courtaulds *BP* 834,312 (28 May 1957)

The fabric is treated with an aqueous solution of NaOH, KOH, alkaline earth or ammonium hydroxide, a basic salt of an alkali metal or an ethanolamine, rinsed, and then treated with a methylated urea- (or melamine-) formaldehyde precondensate, dried, and baked. C.O.C.

Patterns on Fabrics containing Crimped Yarns of Synthetic Polymer Fibres

Heberlein & Co. *BP* 833,145 (Austria 18 April 1957)

Fabric containing elastic crimped yarns of elastic synthetic material has the crimp in them released, e.g. by stretching. The yarn is then set in chosen areas and the crimp restored in the remaining areas, e.g. by allowing the fabric to relax. Finally the fabric is washed and/or steamed in absence of tension. C.O.C.

Crêping Fabrics containing Organic Hydrophobic Fibres

Deering Milliken Research Corpn.

USP 2,907,094 (9 Aug 1952)

True crêpe fabrics containing yarns of highly hydrophobic fibres can be produced by conventional methods providing (1) the fabric is agitated during crêping, and (2) the crêping bath must at the start be below any temperature to which the yarn has been previously subjected, and is raised gradually to full crêping temperature. C.O.C.

Bonded Fibre Fabric

A. H. Drelich and H. W. Griswold

BP 833,697 (U.S.A. 11 Jan 1956)

A carded lap is bonded together by application of many small closely-spaced areas of binding agent. The product resembles a woven fabric in many of its properties. C.O.C.

Impregnation and Coating of Fabrics and Similar Porous Materials

Lewis & Tylor *BP* 833,468 (12 Nov 1956)

The fabric is compressed with expulsion of air, the pressure released, and the fabric then passed through a liquid but solidifiable composition before it expands again as the result of the release of the pressure. C.O.C.

Coloured-coating of Jute Backing for Tufted Carpets

Collins & Aikman Corpn. *USP* 2,908,013 (9 May 1957)

In the manufacture of tufted carpets the backing is liable to become distorted by the tufting needles sticking in the yarn of the backing, in addition when the carpets are dyed the backing is dyed to a different hue and/or depth than the pile. These difficulties are overcome by coating the backing fabric, before tufting, with a latex material containing a colorant which will give the backing the same colour as the pile after it is dyed. This coating is applied to the top surface of the backing, i.e. the side on which the tufts are placed. The underside is given a coating to hold the pile in position. C.O.C.

Leather Substitute

Goppinger Kaliko- und Kunstleder-Werke

BP 834,938 (Germany 18 April 1957)

A product having a chamois leather finish is obtained by coating cloth or other base with a mixture of cork meal and a solution containing the components for a polyurethane resin, e.g. a solution of polyesters and polyisocyanates, and then baking to cure the resin. C.O.C.

XI—PAPER AND OTHER CELLULOSIC PRODUCTS

Modified Artificial Fibres and Films (VI p. 518)

X-Ray Study of the Interaction between Paper and Binding Constituents of Printing Inks (IX p. 521)

Modifying Fibres or Films of Natural or Regenerated Natural Polymers (X p. 522)

Impregnation and Coating of Fabrics and Similar Porous Materials (X this page)

XII—LEATHER; FURS; OTHER PROTEIN MATERIALS

Enzymatic Examination of the Structure of the Collagen Macromolecule

P. H. von Hippel, P. M. Gallop, S. Seifter, and R. S. Cunningham

J. Amer. Chem. Soc., **82** (5 June 1960) 2774–2786

Degradation of collagen as ichthycol, citrate-extracted from carp swim bladders, by purified collagenase, has been studied in detail to obtain further insight into collagen macromolecular structure. Kinetics of this proteolysis observed by pH-stat and colorimetric ninhydrin methods below 27°C. have been interpreted in terms of local differences in polypeptide chain configuration in vicinity of the susceptible peptide bond. Structural alterations accompanying this degradation have been observed from consequent changes in viscosity, light-scattering, non-dialysable protein concn. and optical rotation. Results indicate that the molecule remains relatively unchanged in terms of size and helical content during the initial proteolysis. Interpretation of collagen macromolecule is in terms of a rigid multi-stranded, hydrogen-bonded structure. Enzymatic degradation of single strands causes a partial structural collapse by introducing points of increased flexibility but leaving the particle wt. relatively unaltered. F.J.

PATENTS

Water-repellent, Acid- and Alkali-resistant Pliable Leather

DuP *BP* 836,808 (U.S.A. 5 July 1955)

The skin is tanned and fat-liquored and is also, separately from the fat-liquoring, treated after tanning and before finishing with a Werner-complex in which a trivalent nuclear Cr atom is co-ordinated with carboxylic acid groups of > 9 C. In the case of dyed leather, treatment with the complex is best done after dyeing. C.O.C.

Waterproof Leather

C. and J. Clark *BP* 839,360 (18 July 1955)

Leather is treated with a primary or secondary aliphatic amine of > 11 C in presence of a cross-linking agent. Thus semi-chrome side leather was treated in a 10% solution of stearylamine in isopropanol at 50°C. for 40 min. It was then dried at 50°C. and treated for 1 hr. at 50°C. in 8% formalin containing 1%, on total weight of reagents, of 5 N-H_2SO_4. Finally it was dried at room temperature, heated for 1 hr. at 50°C. and then stored at room temperature for several days. C.O.C.

Current Views on the Mechanism of Leather Dyeing (VIII p. 520)

XIII—RUBBER; RESINS; PLASTICS

Colour Changes in Polymers by Irradiation

T.I. (Group Services) *BP* 835,120 (20 July 1956)

Colour changes penetrating beneath the surface are caused in polymers of chlorine-containing monomers by exposing them to the action of high-energy ionising radiation. The process enables a large number of sheets of e.g. poly(vinyl chloride) to have patterns or prints produced on them simultaneously. C.O.C.

Measurement of Flow Properties of Molten Plastics

W. P. Cox *Off. Dig. Fed. Soc. Paint Technology*, **32** (May 1960) 634–647

The use of capillary extrusion rheometers, rotational viscometers, and dynamic test methods to determine the

rheological characteristics of molten polymers is reviewed. Relative advantages and disadvantages of the various instruments in the study of extremely viscous plastic melts are discussed. Current efforts to correlate the results of steady-flow and dynamic tests are reviewed. 27 references. J.W.D.

PATENTS

Treating Plastic Materials to increase their Adhesive Capacity to Inks
A. Sestini *BP* 841,329 (Italy 28 Dec 1955)

Plastic material, particularly polyethylene, is treated in an A.C. field of frequency 8,000–500,000 cycles per sec. C.O.C.

Textured Plastic Materials
Monsanto *BP* 836,080 (3 Feb 1958)

Mixing 0·05–2·50% of liquid water with particles of an extrudable non-cellulosic polymer and continuing mixing under pressure at > 100 c. and above the temperature at which the polymer softens, and then immediately extruding the mixture through a die kept at a temperature at least as high as that of the mixing, yields a continuous structure whose surface is textured or rugose and whose interior may contain small bubbles. The texture of the product can be controlled by varying the amount of water used. C.O.C.

Calendering Synthetic Resins (I p. 504)

Polymers in Mixed Solvents (V p. 517)

Radiation-induced Graft Copolymerisation of Methacrylic Acid to Nylon (VI p. 518)

Mass Coloration of Vinyl Polymers (VI p. 518)

Modified Artificial Fibres and Films (VI p. 518)

XIV— ANALYSIS; TESTING; APPARATUS

Polarography of Azo Dyes
T. Iijima and M. Sekido
J.S.D.C., **76** (June 1960) 354–355

Coal-tar Colours. XXIII— D&C Red No. 19 (C.I. Basic Violet 10): Identification and Determination of Triethylrhodamine and 2-(2-Hydroxy-4-diethylaminobenzoyl)benzoic Acid in Commercial D&C Red No. 19
C. D. Ritchie, J. A. Wenninger, and J. H. Jones
J. Assoc. Offic. Agr. Chemists, **42** (1959) 720–724
Chem. Abs., **54** (25 March 1960) 5345

The two compounds mentioned in the title were identified in 19 commercial samples of D&C Red No. 19 by described methods of partition chromatography and spectrometric procedures. Preparation of standard compounds is described. C.O.C.

Quantitative Estimation of Silk in Mixtures
E. Frieser *Textil-Rund.*, **16** (May 1960) 238–248

Ten chemical separation methods are considered in relation to unions with cotton, wool and regenerated protein, viscose rayon, cellulose acetate, polyamide and polyvinyl chloride fibres. Corrections for each case are given. S.R.C.

Preparation of Three-dimensional Replicas of Wrinkled Specimens of Fabrics; their Use as Standards for Assessing Wrinkling of Shirts and Shirting Fabrics after Washing and Drying
Z. M. Sudnik *J. Textile Inst.*, **51** (June 1960) T 227–T 239

Graded standards made from blocks of polyester resin whose surfaces are replicas of wrinkled fabrics are used to assess wrinkling of shirts and shirting fabrics after washing and drying. C.O.C.

An Approach to Automation of a Crease Recovery Tester *Amer. Dyestuff Rep.*, **49** (2 May 1960) 302–304

An account of an automatic instrument and comparisons of results obtained with it with those obtained by use of a Monsanto Wrinkle Recovery Tester. C.O.C.

Testing the Microbiological Rotting Resistance of Textile Materials
R. Ashcroft and W. A. Bell
J. Textile Inst., **51** (May 1960) T 175–T 189

The method described is a modification of the conventional soil-burial test. Strips of cloth are laid across bands of soil on glass plates, and are incubated under controlled conditions. The testing arrangement is compact and the samples are visible throughout the test. Experiments to assess the uniformity of the biological conditions and to examine the effect of variations in incubation conditions are also described. S.B.D.

Flammability of Fabrics: Comparison Between Two Methods of Measurement
H. G. Wraight and P. H. Thomas
J. Textile Inst., **51** (May 1960) T 203–T 207

Rates of spread of flame up fabrics both vertically and at an angle of 45° are given and the relationship between the two methods of tests making use of these different orientations of the fabric is discussed. S.B.D.

Microscopic Examination of Faults in Textiles
N. Bigler *S.V.F. Fachorgan*, **15** (April 1960) 251–259

Describes microscopical examination using incident and transmitted light of typical faults caused by physical and chemical agencies. Advantages of varying mounting media in the preparation of microscope slides are discussed. Procedure is given for preparing fabric-surface replicas in gelatin for inspection under a microscope. L.A.T.

Physical Measurement of Colour
A. N. Derbyshire
J. Soc. Leather Tr. Chem., **44** (June 1960) 286–301

The effects of quality of illumination, reflectance, behaviour of the object, and characteristics of the eye in determining the colour of an object are discussed and demonstrated. The C.I.E. system of colour measurement is outlined and instruments for using this system are described. The potential value of such measurements to industrial users of colours are considered and illustrated by an outline of recent experimental work on colour standardisation and colour match prediction. 10 references. C.O.C.

Measurement of Flow Properties in the Adhesives Industry
H. L. Jaffe *Off. Dig. Fed. Soc. Paint Technology*, **32** (May 1960) 629–633

Brief review of instruments used; some are specially designed, others are common to other industries. J.W.D.

***Rf* Values of Nitro-derivatives of Aromatic Hydrocarbons** *J. Chromatography*, **3** (June 1960) D37

Rf values of some di- and tri-nitro derivs. of benzene, toluene, *o*-, *m*- and *p*-xylenes, ethylbenzene and mesitylene, obtained by J. Franc and J. Knížek, *Coll. Czechoslov. Chem. Communs.*, **24**, 2299 (1959) are listed together with solvent, type of paper and detection method. F.J.

Aspects of Bromophenol Blue Staining Deduced from Filter-paper Spot Tests
G. G. Selman *J. Chromatography*, **3** (June 1960) 531–535

Experimental work using bromophenol blue (I) in various media for the estimation of low mol.wt. organic cpds. of biological importance as spots on filter-paper is described. One method for carrying out spot test detects thiol groups in cysteine, the imidazole ring, provided the 9-nitrogen position is not substituted, and thiamine. Comparison of different staining methods with (I) using low mol.wt. amino acids, etc. leads to relevant conclusions in its use as stain for proteins on filter-paper or starch gel. Suggested also that Naphthalene Black 12B 200 (C.I. 20470) may be superior to (I) in comparison of proteins of widely different amino-acid composition on account of lack of specificity. F.J.

Aluminium and Aluminium-based Paints and Their Analysis (IV p. 510)

Effect of Cellulose on Cotton Fibre Microstructure (VI p. 517)

Mechanical Properties of Feather and Down Fibres (VI p. 518)

Measurement of Flow Properties of Molten Plastics (XIII p. 523)

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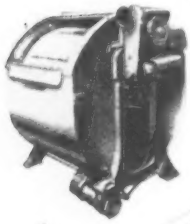

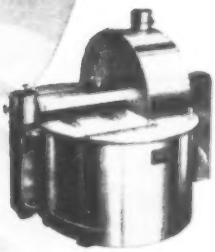

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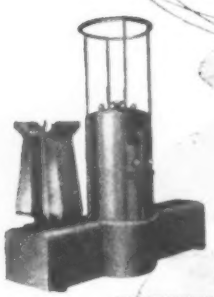

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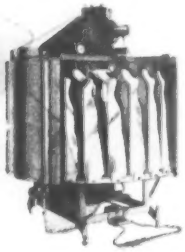

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